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16. ABSTRACT

The report discusses the control of accidental releases of sulfur dioxide (SO2) to the atmosphere. SO2 has an IDLH (immediately dangerous to life and health) concentration of 100 ppm, making it an acute toxic hazard. Reducing the risk associated with an accidental release of SO2 involves identifying some of the potential causes of accidental releases that apply to the processes that use SO2. This manual identifies examples of potential causes and measures that may be taken to reduce the accidental release risk. Such measures include recommendations on: plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided. Headlines of accidental releases of toxic chemicals at Bhopal and Chernobyl have added to the current public awareness of toxic release problems. As a result of other, perhaps less dramatic, incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this series of manuals.

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ABSTRACT

Recent headlines of accidental releases of toxic chemicals at Bhopal and Chernobyl have created the current public awareness of toxic release problems. As a result of other, perhaps less dramatic incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Sulfur dioxide has an IDLH (Immediately Dangerous to Life and Health) concentration of 100 ppm, which makes it an acute toxic hazard.

Reducing the risk associated with an accidental release of sulfur dioxide involves identifying some of the potential causes of accidental releases that apply to the processes that use sulfur dioxide. In this manual, examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided.

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SECTION 1
INTRODUCTION

1.1 BACKGROUND

The consequences of a large release of a toxic chemical can be devastating. This was clearly evidenced by the release of a cloud of toxic methyl isocyanate in Bhopal, India on December 3, 1984, which killed approximately 2,000 people and injured thousands more. Prior to this event, there had been other, perhaps less dramatic, releases of toxic chemicals, but the Bhopal incident precipitated the recent public concern for the integrity of process facilities which handle hazardous materials.

Recognizing the fact that no chemical plant is free of all release hazards and risks, a number of concerned individuals and organizations have contributed to the development of loss prevention as a recognized specialty area within the general realm of engineering science. Interest in reducing the probability and consequences of an accidental release of sulfur dioxide prompted the preparation of this manual. Furthermore, a series of manuals is planned which will address the prevention and control of a large release of any toxic chemical. The subjects of the other manuals planned for the series include:

- A user's guide,
- Prevention and protection technologies,
- Mitigation technologies, and
- Other chemical specific manuals such as this one.

The manuals are based on current and historical technical literature, and they address the design, construction, and operation of chemical process facilities where accidental releases of toxic chemicals could occur. Specifically, the user's guide is intended as a general introduction to the subject of toxic chemical releases and to the concepts which are discussed in more detail in the other manuals. Prevention technologies are applied to the design and operation of a process to ensure that primary containment is not breached. Protection technologies capture or destroy a toxic chemical involved in an incipient release after primary containment has been breached but before an uncontrolled release occurs, while mitigation technologies reduce the consequences of a release once it has occurred.

Historically, there do not appear to have been any significant releases of sulfur dioxide in the United States. Major incidents elsewhere involving sulfur dioxide also do not appear to have been common.

1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to provide technical information about sulfur dioxide with specific emphasis placed on the prevention of accidental releases of this chemical. This manual addresses technological and procedural issues, related to release prevention, associated with the storage, handling, and process operations involving sulfur dioxide.

This manual is intended as a summary manual for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle, or generate sulfur dioxide. It is not intended as a specification manual, and the reader is often referred to additional technical manuals and other information sources for more complete information on the topics discussed. Other sources of information include manufacturers and distributors of sulfur dioxide in addition to technical literature on design, operation, and loss prevention in facilities which handle toxic chemicals.

1.3 USES OF SULFUR DIOXIDE

Sulfur dioxide is a significant commodity chemical, produced by burning sulfur bearing ores or elemental sulfur in air, or by recovery from stack gases to meet clean air requirements. Numerous references in the technical literature provide information on both the manufacture and uses of sulfur dioxide.

The dominant use of sulfur dioxide is as a captive intermediate in the production of sulfuric acid. Its other major uses include chemical manufacture (primarily sulfites), food processing (primarily corn), pulp and paper manufacture, water and waste water treatment, and metallurgical applications. Minor uses are found in a variety of industries including the refrigeration, food preservation, bleaching, fumigating, and petroleum industries.

1.4 CONTENTS OF THIS MANUAL

Following this introductory section, the remainder of this manual presents technical information on specific hazards and categories of hazards for sulfur dioxide releases and their control. As stated previously, these are examples only and are representative of only some of the hazards that may be related to accidental releases. The physical, chemical, and toxicological properties of sulfur dioxide which create or enhance the hazards of an accidental release are presented in Section 2. In Section 3, the manufacture, consumption, and storage of sulfur dioxide are discussed, and the release hazards associated with these operations are identified. Potential causes of releases, including those identified in Section 3, are summarized in Section 4. Section 5 contains detailed information about hazards prevention and control. Topics included in this section are process and physical plant designs, protection and mitigation technologies, operating and maintenance practices, and illustrative costs.

SECTION 2
CHEMICAL CHARACTERISTICS

This section describes the physical, chemical, and toxicological properties of sulfur dioxide as they relate to accidental release hazards.

2.1 PHYSICAL PROPERTIES

Sulfur dioxide (SO_2) is a colorless gas with a characteristic pungent odor and taste. Although the gas is relatively inert and stable, it is toxic and highly irritating. Its more important physical and chemical properties are presented in Table 2-1.

The solubility of sulfur dioxide gas in water is 36 volumes per volume of water at 68 °F. It is also very soluble (several hundred volumes per volume of solvent) in a number of organic solvents such as acetone, other ketones, and formic acid (1).

Because of the low boiling point, and because the gas is considerably heavier than air, spills and leaks of liquid sulfur dioxide could result in a vapor cloud or plume that will remain close to the ground, posing a threat to workers and surrounding communities.

Pure liquid sulfur dioxide is a poor conductor of electricity and is only slightly miscible with water (1). The liquid also has a high coefficient of expansion, expanding approximately 10% when warmed from 68 °F to 140 °F (1). Hence, an overpressurization hazard exists if storage vessels have insufficient expansion space or if liquid sulfur dioxide pipelines may be blocked in.

TABLE 2-1. PHYSICAL PROPERTIES OF SULFUR DIOXIDE

		Reference
CAS Registry Number	7446-09-5	
Chemical Formula	SO_2	
Molecular Weight	64.06	
Normal Boiling Point	14.0 °F @ 14.7 psia	1
Melting Point	-98.9 °F	1
Liquid Specific Gravity (H_2O=1)	1.436 @ 32 °F	2
Vapor Specific Gravity (air=1)	2.263 @ 32 °F	1
Vapor Pressure	49.1 psia @ 70 °F	2
Vapor Pressure Equation		3

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 7.28228, a constant
B = 999.900, a constant
C = 237.190, a constant

Liquid Viscosity	0.49 centipoise @ -4 °F and 14.22 psia	4
Solubility in Water at 1 atm, g/100g H_2O		1

32 °F	22.971
50 °F	16.413
68 °F	11.577
86 °F	8.247
104 °F	5.881

(Continued)

TABLE 2-1 (Continued)

		Reference
Specific Heat at Constant Pressure (vapor)	0.149 Btu/(lb-°F) @ 77 °F	1
Specific Heat at Constant Pressure (liquid)	0.327 Btu/(lb-°F) @ 68 °F	4
Latent Heat of Vaporization	167.24 Btu/lb @ 14.0 °F	1
Liquid Surface Tension	28.59 dynes/cm @ 14 °F	4
Additional properties useful in determining other properties from physical property correlations:		
Critical Temperature	315.7 °F	1
Critical Pressure	1,147 psia	1
Critical Density	0.51 lb/ft^3	1
Energy of Molecular Interaction	252 K	5
Effective Molecular Diameter	4.29 Angstroms	5

2.2 CHEMICAL PROPERTIES AND REACTIVITY

Sulfur dioxide is extremely stable to heat, even up to 3600 °F (1). It does not form flammable or explosive mixtures with air. It will, however, react with water or steam to produce toxic and corrosive fumes (6). When the gas dissolves in water it forms a weak acid solution of sulfurous acid (H_2SO_3) which is corrosive and unstable when exposed to heat (7). Sulfurous acid does not exist in the free state, dissociating to the sulfite and bisulfite ions, $SO_3^{=}$ and HSO_3^{-}. The deleterious effect of sulfur dioxide and sulfites in domestic water is the increased corrosivity owing to the lowered pH. However, oxidation of sulfite to sulfate in aqueous solutions uses dissolved oxygen, and this may retard corrosion (6). While the oxidation of sulfite and sulfurous acid to sulfate and sulfuric acid in the atmosphere is an environmental concern, this reaction is too slow to significantly reduce the concentration of sulfur dioxide in a short time period in the event of a large release.

Sulfur dioxide can be reduced by hydrogen to hydrogen sulfide. It also reacts with chlorine to form sulfuryl chloride. Both of these gaseous products are toxic. The reduction of sulfur dioxide to sulfur can be accomplished with H_2S, methane, carbon (coal), and CO (1). The reaction with H_2S will occur at ambient temperatures in the presence of water, but requires high temperatures or a catalyst when sulfur dioxide is in the dry state. Sulfur dioxide is reported to react violently with a number of compounds of which several may be present in facilities which also use sulfur dioxide, e.g., chlorates, Al, and Cr compounds (6,8). The reaction with chlorates produces chlorine, and this has the potential to become an explosive reaction at elevated temperatures (8).

Most metals are resistant to commercial dry liquid sulfur dioxide, dry gaseous sulfur dioxide, and hot gaseous sulfur dioxide containing water vapors above the dew point (1). These include iron, steel, copper, aluminum, and brass. However, these materials are readily corroded by wet sulfur dioxide gas below the dew point. Zinc is also readily oxidized by sulfur dioxide to form ZnS_2O_4.

2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Sulfur dioxide is a toxic, highly irritating gas which can have immediate effects on the eyes, throat, lungs, and skin. The toxicology of sulfur dioxide has been studied through accidental human exposure and through animal studies (9). A concentration of 100 ppm has been designated as the IDLH limit (Immediately Dangerous to Life and Health), which is based on a 30-minute exposure (10). Table 2-2 presents a summary of some of the relevant exposure limits for sulfur dioxide.

The primary health effects from exposure to sulfur dioxide occur in the upper respiratory tract and the bronchi. Chronic exposure may result in nasopharyngitis, fatigue, altered sense of smell, and chronic bronchitis symptoms such as dyspnea on exertion, cough, and increased mucous excretion (10). It may cause edema of the lungs or glottis and can produce respiratory paralysis (6). In concentrations greater than 20 ppm, sulfur dioxide is irritating to the eye and will cause pain, tearing, inflammation, swelling of tissue and possible destruction of the eye (7,8). Acclimation to the effects of sulfur dioxide has been reported to develop quickly as a result of the depression of the tracheobronchial nerve reflexes; this adjustment is not considered to be a beneficial effect because of the possibility that the absence of discomfort merely removes one measure of protection (9). The physical effects of increasing levels of gas concentrations on humans are summarized in Table 2-3 (11).

Sulfur dioxide is not listed in the National Toxicology Program, the International Agency for Research on Cancer, nor the Registry of Toxic Effects of Chemical Substances (1981-82) as a carcinogen or potential carcinogen (12). However, sulfur dioxide has been implicated as a cocarcinogen (promoter) with arsenic (9).

Contact with liquid sulfur dioxide may cause cryogenic burns to the skin in addition to conjunctivitis, corneal burns, and corneal opacity of the eye (7,8,10). It is also reported that high concentrations of sulfite ion in water may cause eczema (6).

TABLE 2-2. EXPOSURE LIMITS FOR SULFUR DIOXIDE

Exposure Limit	Concentration (ppm)	Description	Ref.
IDLH	100	The concentration defined as posing an immediate danger to life and health (i.e., causes irreversible toxic effects for a 30-minute exposure).	10
PEL[a]	5	This concentration was determined by the Occupational Safety and Health Administration (OSHA) to be the time-weighted 8-hour exposure limit which should result in no adverse effects for the average worker.	10
LC_{LO}	400	This concentration is the lowest published lethal concentration for a human over a 5-minute exposure.	6
TC_{LO}	4	This concentration is the lowest published concentration causing toxic effects (irritation).	6

[a] PEL stands for the "permissable exposure limit."

TABLE 2-3. PREDICTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF SULFUR DIOXIDE (7)

ppm	Predicted Effect
0.3-1	Can be detected by taste and smell
3	Easily noticeable odor
6-12	Immediate irritation of nose and throat
20	Eye irritation - ill effects if exposure is prolonged
50-100	Maximum permissible concentration for 30 to 60 minutes exposure
200	Severe toxic effects after one minute
>400	Immediately dangerous to life

SECTION 3
FACILITY DESCRIPTIONS AND PROCESS HAZARDS

This section contains brief descriptions of the processes and facilities for the manufacture, consumption, and storage of sulfur dioxide in the United States. The purpose of this section is to identify major hazards associated with these facilities which may directly or indirectly cause accidental releases. Measures taken for the prevention of these hazards are discussed in Section 5.

3.1 MANUFACTURE (1,2,13)

Sulfur dioxide gas is produced in the United States by several methods which include the combustion of sulfur or pyrites, as a by-product of smelter operations, and as a by-product of other chemical operations. For many of the chemical process applications which require sulfur dioxide gas or sulfurous acid, sulfur dioxide is captively produced by the burning of sulfur or pyrite, FeS_2, and the gas is immediately consumed in the process. The manufacture of liquid sulfur dioxide for commercial sale involves passing the combustion gas into water which dissolves it and certain impurities. This liquor is then heated to drive off the sulfur dioxide, and the liberated gas is dried and liquefied.

Figure 3-1 is a typical flow diagram for the preparation of liquid sulfur dioxide. The sulfur-bearing raw material is fed to the burner where it is combusted with air. The type of burner used is primarily determined by the rate and concentration of sulfur dioxide to be produced and the quality of sulfur to be burned. The sulfur dioxide content of the burner gas is dependent on the equilibrium adiabatic flame temperature and varies from about 6.5% at 1470 °F to about 20% at 3180 °F when the raw material is elemental sulfur (13). After leaving the burner, the heat of combustion is recovered in a

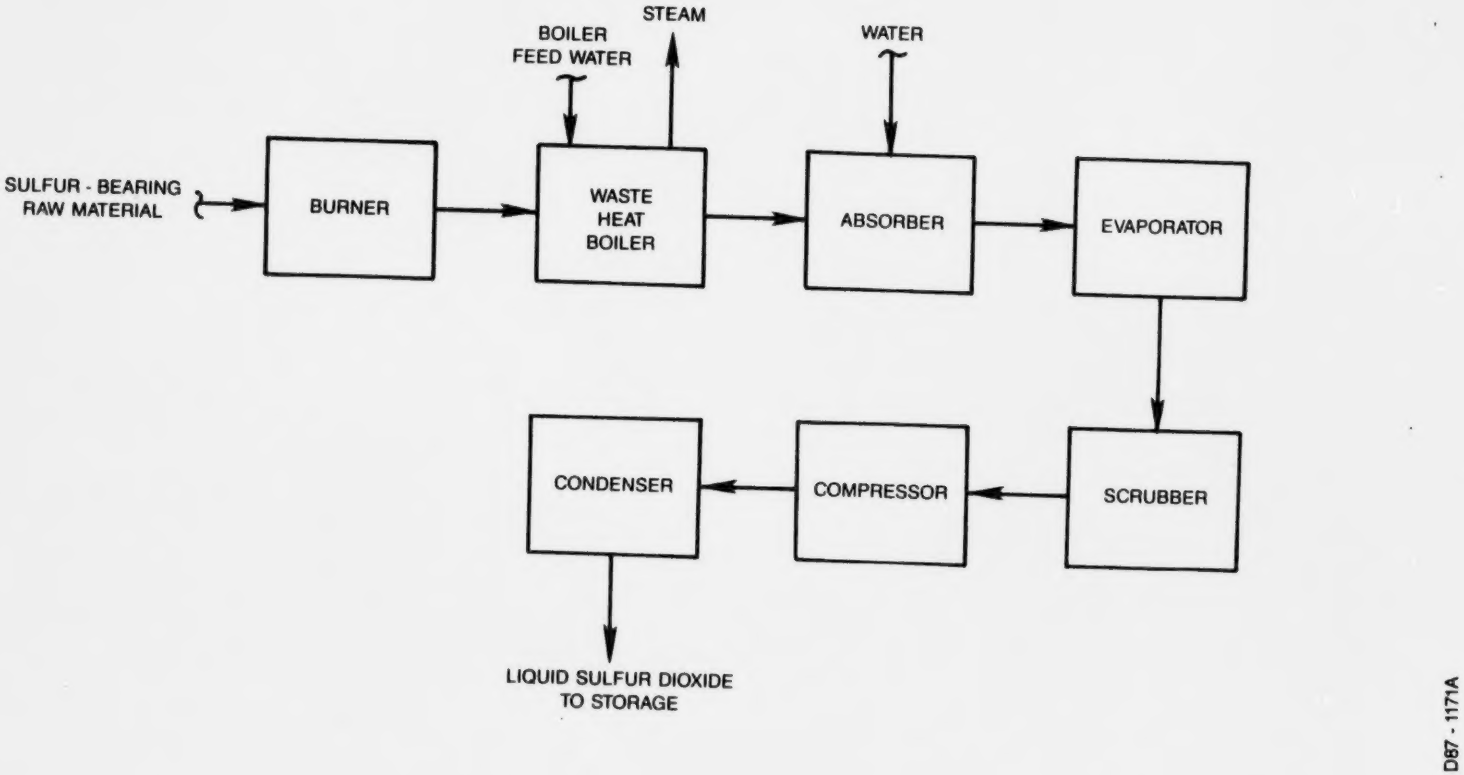

SULFUR - BEARING RAW MATERIAL
BURNER
BOILER FEED WATER
STEAM
WASTE HEAT BOILER
WATER
ABSORBER
EVAPORATOR
SCRUBBER
COMPRESSOR
CONDENSER
LIQUID SULFUR DIOXIDE TO STORAGE
D87 - 1171A

Figure 3-1. Conceptual diagram of typical sulfur dioxide manufacturing process.

waste-heat boiler, after which the combustion gas is further cooled prior to absorption in water. Lead pipes in flowing water are commonly used for cooling the gas. The combustion gas then passes through one or more absorption towers in which the sulfur dioxide and certain impurites are absorbed into water. The resulting liquor is then heated to drive off sulfur dioxide gas. The gas is cleaned and dried with concentrated acid, cooled, compressed, and finally condensed to pure liquid product.

The primary hazard areas in the production of liquid sulfur dioxide are at the latter end of the process where sulfur dioxide is present in pure form. The following potential release hazards may be identified in this portion of the process (excluding the bulk storage system which is discussed in Section 3.4):

- The leakage of moisture into any equipment which handles a large amount of sulfur dioxide with the consequent formation of corrosive sulfurous acid;

- Failure of the sulfur dioxide compressor possibly resulting from a power failure, rotor failure, or excessive stress caused by severe vibrations; and

- A loss of cooling to the sulfur dioxide condenser which results in a pressure buildup and possible equipment failure.

Other release hazards, or possible causes of release, which are general to all sulfur dioxide processing facilities are summarized in Section 4.

3.2 PROCESSING AND CONSUMPTION

The example processes discussed in this section represent many of the primary uses of sulfur dioxide and include the production of sulfuric acid, the sulfonation of alkanes, pulp and paper manufacture, water and waste water treatment, and solvent extraction. Sulfur dioxide is also used in the manufacture of a variety of important industrial chemicals which are too numerous to discuss individually. Many of these products are listed in Table 3-1.

3.2.1 Manufacture of Sulfuric Acid (1)

Sulfuric acid is produced by the contact process. Different variations of this process use a wide range of sulfur-bearing raw materials. The most common raw material is elemental sulfur. The process produces gaseous sulfur dioxide by sulfur combustion, followed by catalytic conversion of the sulfur dioxide to sulfur trioxide (SO_3), and absorption of the SO_3 into concentrated sulfuric acid.

Regardless of the source of sulfur, the first step in the contact process produces a continuous, contaminant-free gas stream containing appreciable sulfur dioxide and some oxygen. A dry gas stream entering the catalytic converters is desirable; the air used for burning elemental sulfur is generally predried, while other processes dry the sulfur dioxide stream after it leaves the combustion chamber. Sulfur trioxide is produced from the sulfur dioxide by catalytic conversion, and it is subsequently absorbed into a circulating stream of 98-99% H_2SO_4 at approximately 158-176 °F.

Figure 3-2 illustrates the contact process for a double-absorption sulfur-burning plant. Single-absorption plants used to be the industry norm, but stricter controls on residual sulfur dioxide emissions necessitated an intermediate absorption step to effect overall sulfur dioxide conversions of 99.5-99.8% in the newer plants. However, most existing facilities chose to add a tail-gas unit instead of modifying the process with an additional absorption step.

TABLE 3-1. SULFUR DIOXIDE REACTION PRODUCTS (14)

- sulfur dioxide
- ammonium sulfite
- ammonium thiosulfate
- hydroxylamine sulfate
- potassium bisulfite
- potassium sulfate
- potassium thiosulfate
- sodium bisulfite
- sodium persulfate
- sodium sulfite
- sodium bisulfate
- sodium thiosulfate
- sodium hydrosulfite
- sulfurous acid
- sulfuryl chloride
- pyrosulfuryl chloride
- zinc sulfide
- zinc hydrosulfite
- zinc formaldehyde sulfoxylate
- sulfonamides:
  - sulfadiazine
  - sulfanilimide
  - sulfapyridine
  - sulfathiazole
  - sulfolane

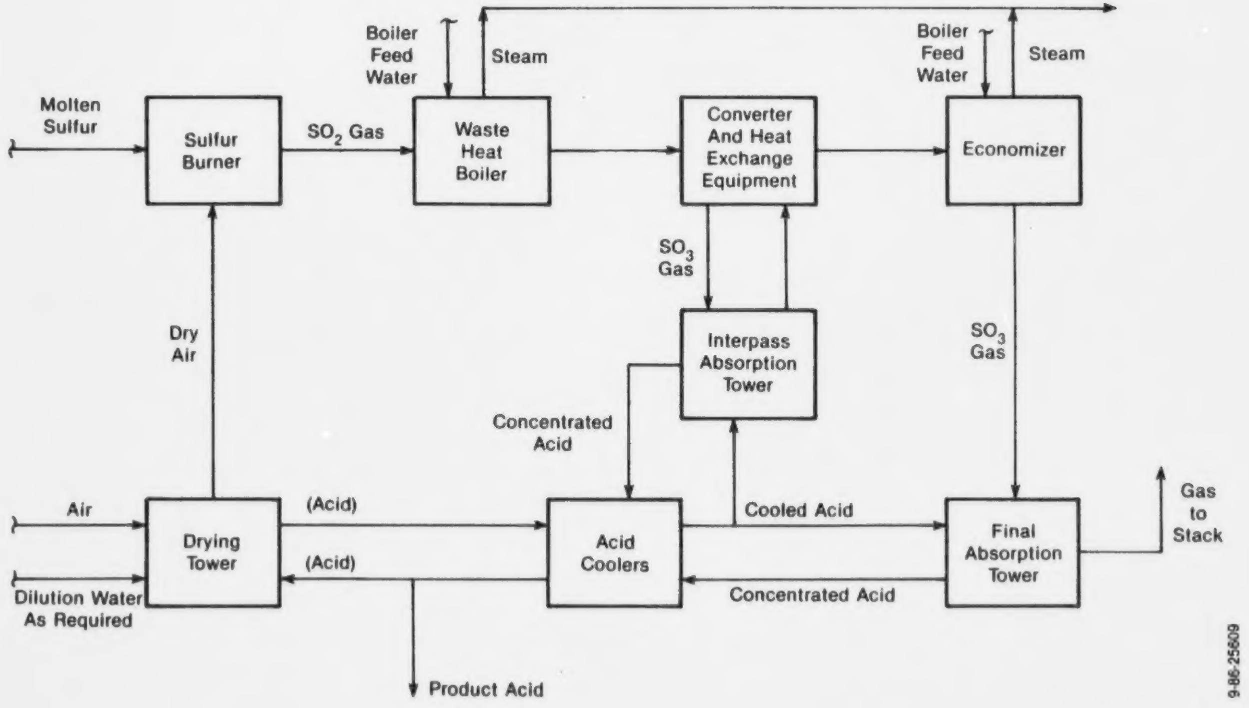

Molten Sulfur
Sulfur Burner
SO_2 Gas
Boiler Feed Water
Steam
Waste Heat Boiler
Converter And Heat Exchange Equipment
Boiler Feed Water
Steam
Economizer
SO_3 Gas
Interpass Absorption Tower
SO_3 Gas
Dry Air
Concentrated Acid
Air
Drying Tower
Dilution Water As Required
(Acid)
(Acid)
Acid Coolers
Cooled Acid
Concentrated Acid
Final Absorption Tower
Gas to Stack
Product Acid
9-86-25609

Figure 3-2. Conceptual diagram of typical double-absorption sulfuric acid process.

The maximum concentration of sulfur dioxide present at any point in the process is in the gas stream exiting the sulfur combustion chamber. Typical sulfur dioxide concentrations range from 4-11 vol%. Since sulfur dioxide is only present at this concentration between the sulfur burner and the catalytic converters, the pieces of equipment in this part of the process are the only potential sources of a hazardous release of sulfur dioxide under normal operating conditions. Some general causes of equipment failure which may lead to a large release of sulfur dioxide are discussed in Section 4.

If a process upset were to occur such that the conversion level of sulfur dioxide to SO_3 was greatly reduced, the process stream beyond the catalytic converters would contain a considerable quantity of sulfur dioxide. One possible upset is a loss of temperature control in the converters resulting in a significant temperature increase which would cause the equilibrium in the oxidation reaction to become less favorable toward SO_3 formation.

Because of the exothermic nature of the oxidation of sulfur dioxide to SO_3, overheating resulting in overpressure is also a potential hazard in the catalytic converters with the consequent possibility of leaks developing or, in the worst case, equipment failure and loss of containment.

3.2.2 Sulfonation of Alkanes (15)

Sulfur dioxide is used as a reagent in several sulfation and sulfonation processes which chemically introduce the SO_3 group into organic molecules. Sulfonated and sulfated organics have many "surface-active" applications, e.g., detergents, dyes, and medicinals, because of their unique properties of solubility, emulsification, wetting, and foaming.

In most sulfation and sulfonation processes, the actual sulfonating agent is either oleum, sulfuric acid, or sulfur trioxide. The use of sulfur dioxide in these processes is not widespread in industry. However, one sulfonation process employed in the U.S. does use significant quantities of liquid sulfur dioxide. The sulfur dioxide in this process serves as a diluent for oleum (fuming sulfuric acid) which contains 60-75% free sulfur trioxide. It is necessary to dilute the sulfur trioxide, because acid of this strength will severely char and degrade the alkane being sulfonated. As the reaction is highly exothermic, cooling requirements also become very important at high sulfur trioxide concentrations. If the sulfur dioxide is supplied in sufficient quantities it will serve as the cooling medium for the process. Because the sulfur dioxide does not participate as a reactant in the sulfonation, it is separated from the reaction products and recycled to the process.

Figure 3-3 is a flow diagram of a typical sulfonation process which uses sulfur dioxide as a diluent and a refrigerant. The sulfur dioxide and oleum are pumped from storage to an agitated weigh tank. The weight ratio of sulfur dioxide to oleum is approximately 7 to 1, and the quantity of sulfur dioxide used corresponds to a weight ratio of about 2 to 4 parts of sulfur dioxide to one part of the alkane subsequently added. The process may be adapted for continuous or batch sulfonation depending on the way the reactants are fed to the sulfonator. For batch operation, the alkane is charged to the reactor, and the diluted oleum charge is fed to the agitated sulfonator at a controlled rate to avoid overheating. For continuous operation, both the alkane and the oleum are pumped continuously at controlled rates to the sulfonator, and the sulfonated product is continuously withdrawn. The flow rates of the reactants may be regulated by a valve which is controlled by the temperature of the reactants in the sulfonator. This is done to maintain a reaction temperature of about 20-65 °F. The heat of reaction is continuously removed from the reactor by the vaporization and release of sulfur dioxide. The vented sulfur dioxide passes through a liquid trap where any liquid materials are separated and allowed to drain back to the sulfonator. The gas stream is then scrubbed in a solution of 93-100% sulfuric acid before passing to one or more compressors. After compression and condensation, the sulfur dioxide is returned to storage for reuse in the process.

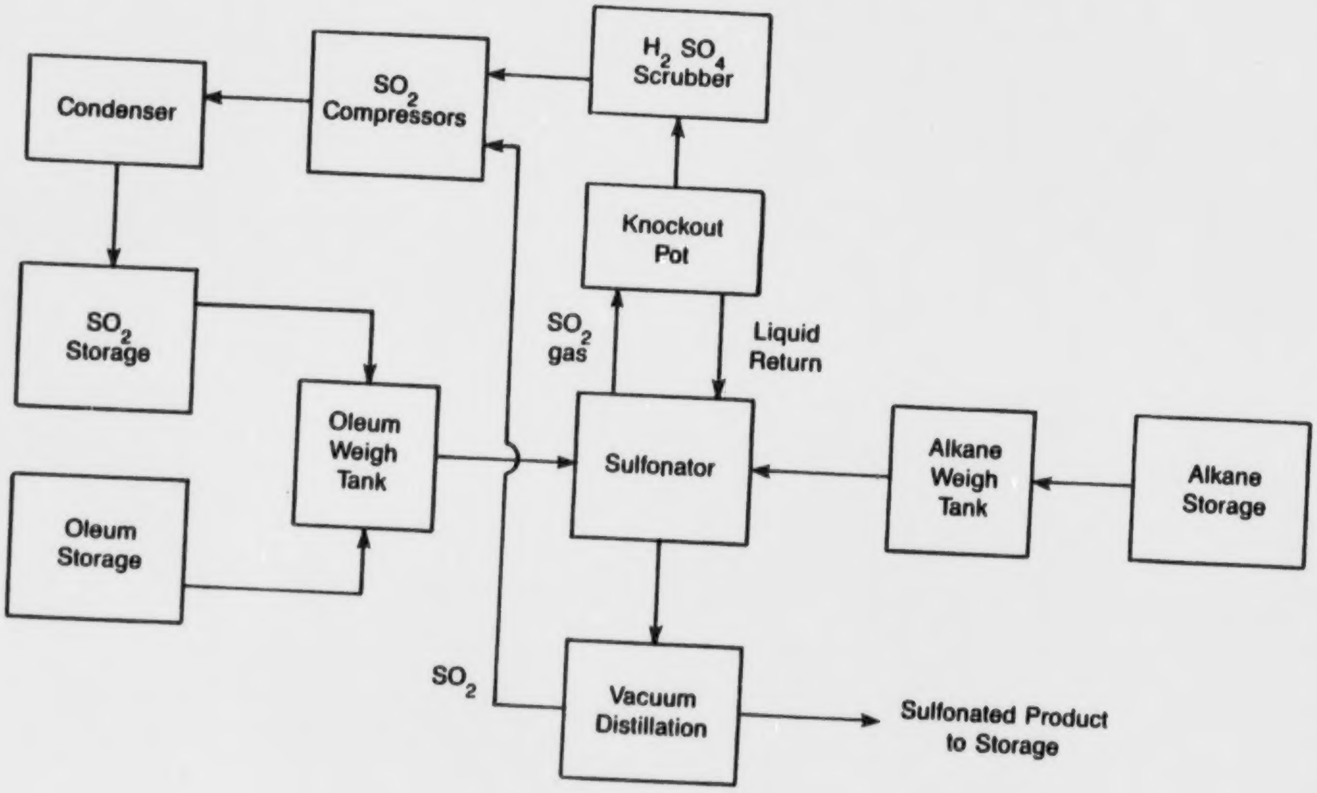

H_2SO_4 Scrubber
SO_2 Compressors
Condenser
Knockout Pot
SO_2 gas
Liquid Return
SO_2 Storage
Oleum Weigh Tank
Sulfonator
Alkane Weigh Tank
Alkane Storage
Oleum Storage
SO_2
Vacuum Distillation
Sulfonated Product to Storage

Figure 3-3. Conceptual diagram of typical sulfonation process.

There are a number of areas in this process where the sulfur dioxide is present in high concentrations or nearly pure form. Because the sulfur dioxide is not consumed in the sulfonation reaction, the possibility of a large release of this chemical is greater than what might exist in a process where the sulfur dioxide is consumed as a reactant. From a sulfur dioxide release perspective, critical areas of the process include the sulfur dioxide storage and feed systems, the sulfonator, and the sulfur dioxide recovery section (including the sulfur dioxide compressors, condenser and storage tank). Examples of possible causes of a large release include the following:

- If moisture leaks into the system, equipment which handles a large amount of sulfur dioxide may be corroded by the sulfurous acid formed and be weakened to the point of sudden rupture;

- If there is a failure in the feed control system, a runaway reaction may result which causes a buildup of pressure exceeding the design pressure of the sulfonator; and

- A loss of cooling to the sulfur dioxide condenser may also result in a pressure buildup and equipment failure.

If the oleum feed is too concentrated, the exothermic sulfonation reaction will proceed too quickly, resulting in a temperature rise in the reactor and a consequent increase in pressure. Because the sulfur dioxide recovery section involves relatively pure streams of sulfur dioxide, this section of the process represents a potential hazard area. Overpressurization of a condenser may occur if the cooling system fails. Although this may not lead to catastrophic equipment failure, leaks of sulfur dioxide into the plant cooling water could result in the formation of corrosive levels of sulfurous acid.

3.2.3 Sulfur Dioxide in the Pulp and Paper Industry

Sulfite Pulping (16,17,18)--

One of the primary uses of sulfur dioxide is in the manufacture of chemicals (see Table 3-1) of which sulfites represent a majority of the sulfur dioxide consumed. One major application of sulfite solutions is the sulfite pulping process used in the manufacture of paper. There are a number of variations of the sulfite pulping process, and there are also many other pulping processes, encompassing both mechanical and chemical methods, which do not require the use of sulfur dioxide.

The purpose of pulping is to separate the cellulose fibers from the matrix of lignin which cements them together. The usual sulfite process is a chemical method which consists of digesting the wood by "cooking" it in an aqueous bisulfite solution (usually Ca, Mg, Na, or NH_3) and an excess of sulfur dioxide. Recently, multi-stage pulping processes have been introduced in which the stages differ from each other in the cooking liquor used. Liquid sulfur dioxide is used in some of these processes as the cooking liquor in the second stage (16).

In the preparation of the sulfite solution, gaseous sulfur dioxide is typically generated by burning molten sulfur in either rotary or spray burners. The gas exiting the burner usually contains about 17% sulfur dioxide with the remainder of the gas consisting mostly of nitrogen and a small amount of oxygen. This gas is cooled from a temperature of about 1800 °F to between 77 °F and 158 °F depending on the desired pH of the sulfite liquor. The cooling process generally involves a horizontal, vertical, or pond cooler consisting of a system of pipes surrounded by water.

The sulfite "cooking acid" is prepared by the absorption of the gaseous sulfur dioxide in aqueous solutions containing calcium, magnesium, sodium, or ammonium compounds. This is accomplished in a series of two or more absorption towers or acid-making tanks for $Mg(HSO_3)_2$. Sulfur dioxide solubility is a function of the temperature, pressure, and pH during absorption. System absorption efficiencies for the different absorption systems used in industry range from 97% to greater than 99% (18).

The portions of the sulfite pulping process which involve significant quantities of sulfur dioxide include the gas exiting the sulfur burners and the recovery of sulfur dioxide from the spent cooking liquor. Potential hazards associated with the process gas stream involve the piping between the sulfur burners and the absorption towers including the gas cooling section. Because water is used as the cooling medium, a release of sulfur dioxide gas would result in the formation of corrosive sulfurous acid. Some general causes of equipment failure (including piping systems) are discussed in Section 4.

A number of sulfur recovery procedures are employed in the pulping industry. Some of these processes include a sulfur dioxide stripping operation which produces a nearly pure stream of gaseous sulfur dioxide. While the recovered sulfur dioxide is generally fed back to the sulfur dioxide absorption towers, it may also be combined with H_2S and fed to a Claus unit or used to make liquid sulfur dioxide for use in a multi-stage pulping process (16). This type of system is illustrated in Figure 3-4 which shows the preparation of the cooking acid and recovery of the sulfur from the spent solution. Potential hazards associated with the sulfur dioxide recovery section depend on the process employed by the particular pulping operation. Some possible causes of release general to many sulfur dioxide applications are discussed in Section 4.

For multi-stage processes which use liquid sulfur dioxide, the storage system constitutes one of the potential sources of a hazardous release. The general hazards associated with the storage of sulfur dioxide are discussed in Section 3.4.

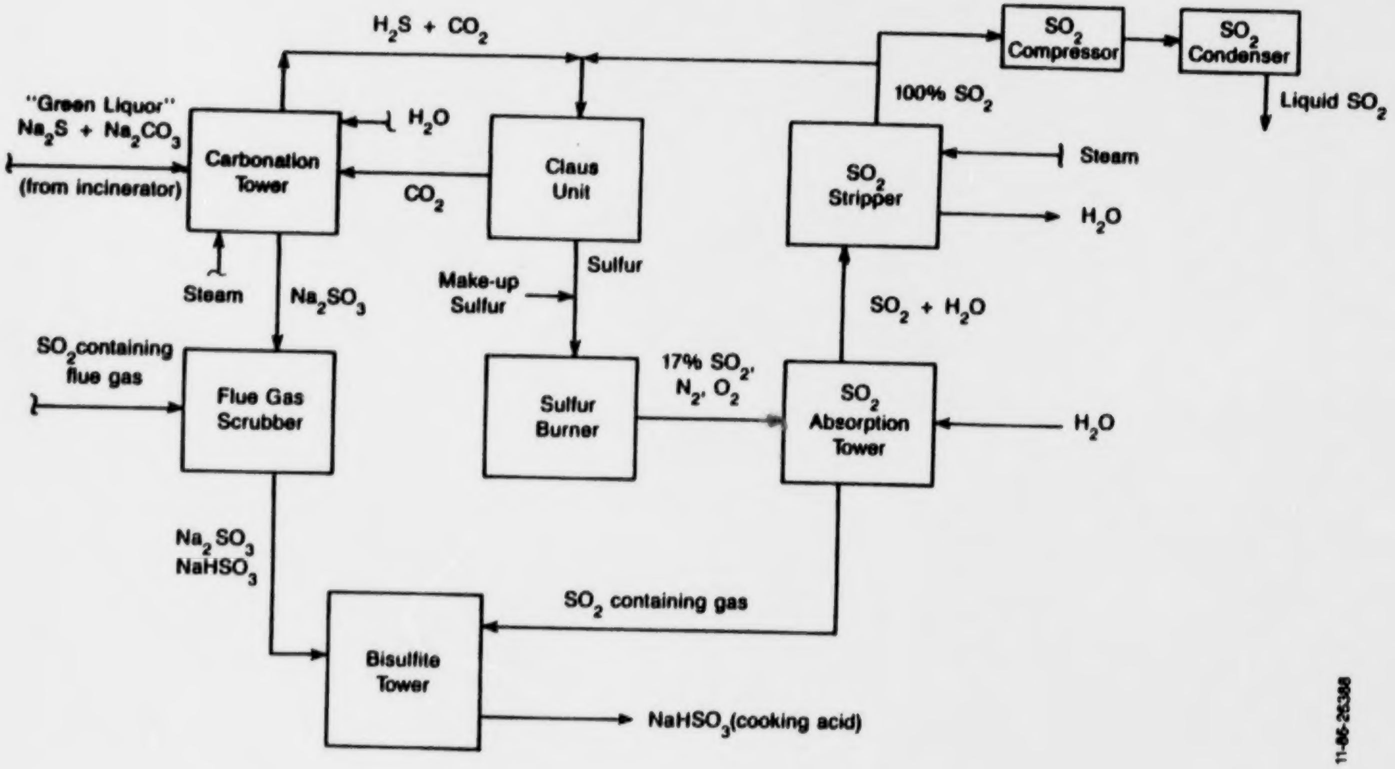

H$_2$S + CO$_2$
SO$_2$ Compressor
SO$_2$ Condenser
Liquid SO$_2$
"Green Liquor"
Na$_2$S + Na$_2$CO$_3$
(from incinerator)
Carbonation Tower
H$_2$O
Claus Unit
CO$_2$
100% SO$_2$
SO$_2$ Stripper
Steam
H$_2$O
Steam
Na$_2$SO$_3$
Make-up Sulfur
Sulfur
SO$_2$ + H$_2$O
SO$_2$containing flue gas
Flue Gas Scrubber
Sulfur Burner
17% SO$_2$, N$_2$, O$_2$
SO$_2$ Absorption Tower
H$_2$O
Na$_2$SO$_3$
NaHSO$_3$
SO$_2$ containing gas
Bisulfite Tower
NaHSO$_3$(cooking acid)
11-86-26388

Figure 3-4. Conceptual diagram of sulfite cooking liquor preparation and sulfur recovery process.

Preparation of Chlorine Dioxide (16,19,20,21)--

Chlorine dioxide is used in the pulp bleaching process, not only to increase the brightness, but also to improve pulp strength, decrease color reversion, and to make possible the recovery of bleach plant effluents. Because this chemical is explosive at higher concentrations, it cannot be transported in any concentrated form; thus, it is generally produced at the pulp mill immediately before use.

Chlorine dioxide is manufactured from sodium chlorate in strong acid solution, usually sulfuric. A reducing agent is required to reduce the chlorate ion to chlorine dioxide. Three reducing agents are used for this purpose in industry, one of which is sulfur dioxide. Figure 3-5 is a flow diagram for a typical process which uses sulfur dioxide as the reducing agent.

The reaction is carried out in a cylindrical vessel which contains a solution of sodium chlorate, sulfuric acid, and chloride ions. Sulfur dioxide and chlorine are pumped from their respective liquid storage vessels to the evaporators. The two gas streams are diluted with nitrogen (air is also sometimes used) and mixed prior to entering the reactor through a sparger. The effluent gas exiting the reactor contains chlorine dioxide, chlorine gas, and nitrogen. Sodium chlorate and sulfuric acid are recovered from the effluent solution and recycled back to the reactor.

The reaction of sulfur dioxide with chlorate is highly exothermic. The temperature of the reaction must be carefully controlled to avoid a runaway reaction. For this reason, the volume percent of sulfur dioxide in the gas mixture must be maintained below 18% to avoid an excessive heat of reaction. The metering of reagents and the flow of dilution gas have to be accurate. The process hazard from an excess of sulfur dioxide in the feed or the loss of cooling to the reactor is the production of too much chlorine dioxide. At higher concentrations this chemical quickly decomposes to chlorine gas and

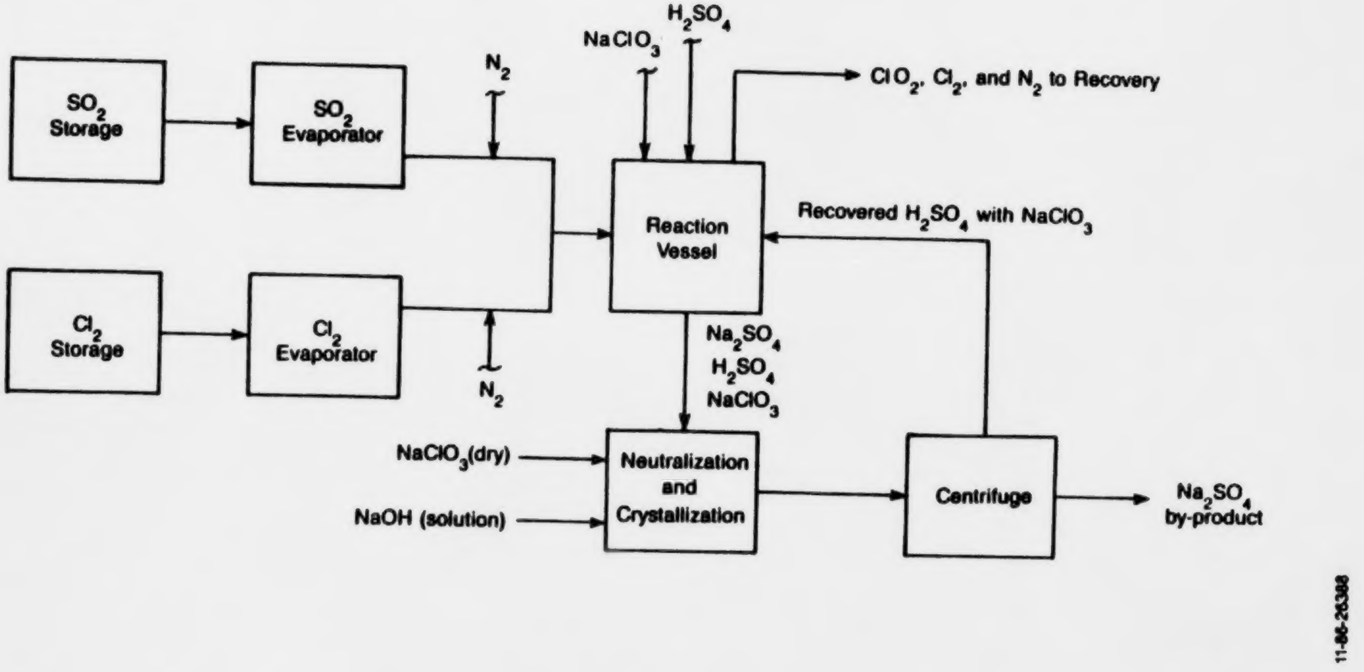

SO$_2$ Storage
SO$_2$ Evaporator
Cl$_2$ Storage
Cl$_2$ Evaporator
N$_2$
N$_2$
NaClO$_3$
H$_2$SO$_4$
Reaction Vessel
ClO$_2$, Cl$_2$, and N$_2$ to Recovery
Recovered H$_2$SO$_4$ with NaClO$_3$
Na$_2$SO$_4$
H$_2$SO$_4$
NaClO$_3$
NaClO$_3$(dry)
NaOH (solution)
Neutralization and Crystallization
Centrifuge
Na$_2$SO$_4$ by-product
11-86-26388

Figure 3-5. Conceptual diagram of typical chlorine dioxide manufacturing process.

oxygen with explosive force. Therefore, most operations incorporate a temperature shutdown switch into the control system which shuts off the feed in the event of an unacceptable rise in reaction temperature.

The prevention of an explosive concentration of chlorine dioxide gas is the major process concern in the production of this chemical, but the release of a large amount of sulfur dioxide is not the primary hazard of such an explosion. This is because the release of a large quantity of chlorine dioxide and chlorine gas would be a greater danger to workers and the surrounding community. However, the ratio of sulfur dioxide to chlorine gas in the feed may be as high as 10 to 20:1 (20). Hence, if the feed system is not shut off at the time of a reactor explosion, the sulfur dioxide released from a venting feed line could, in this case, pose a serious hazard in itself.

As liquid sulfur dioxide is used as the source of the gaseous sulfur dioxide feed, potential hazards which may result in a large release of sulfur dioxide involve the storage facilities, the evaporator, and the feed system to the reactor. Hazards associated with the storage of liquid sulfur dioxide are discussed in Section 3.4. Other general equipment hazards are discussed in Section 4.

Preparation of Sodium Dithionate (18)--

Sodium dithionate is also used in the pulp bleaching process. It is produced at the mill site by the reaction of sulfur dioxide or bisulfite with sodium borohydride in an alkaline medium. As the sulfur dioxide is consumed in the reaction, the hazards which may lead to a large release of sulfur dioxide are the hazards associated with the storage and feed systems for this chemical. General hazards pertaining to these areas are discussed in Sections 3.4 and 4.

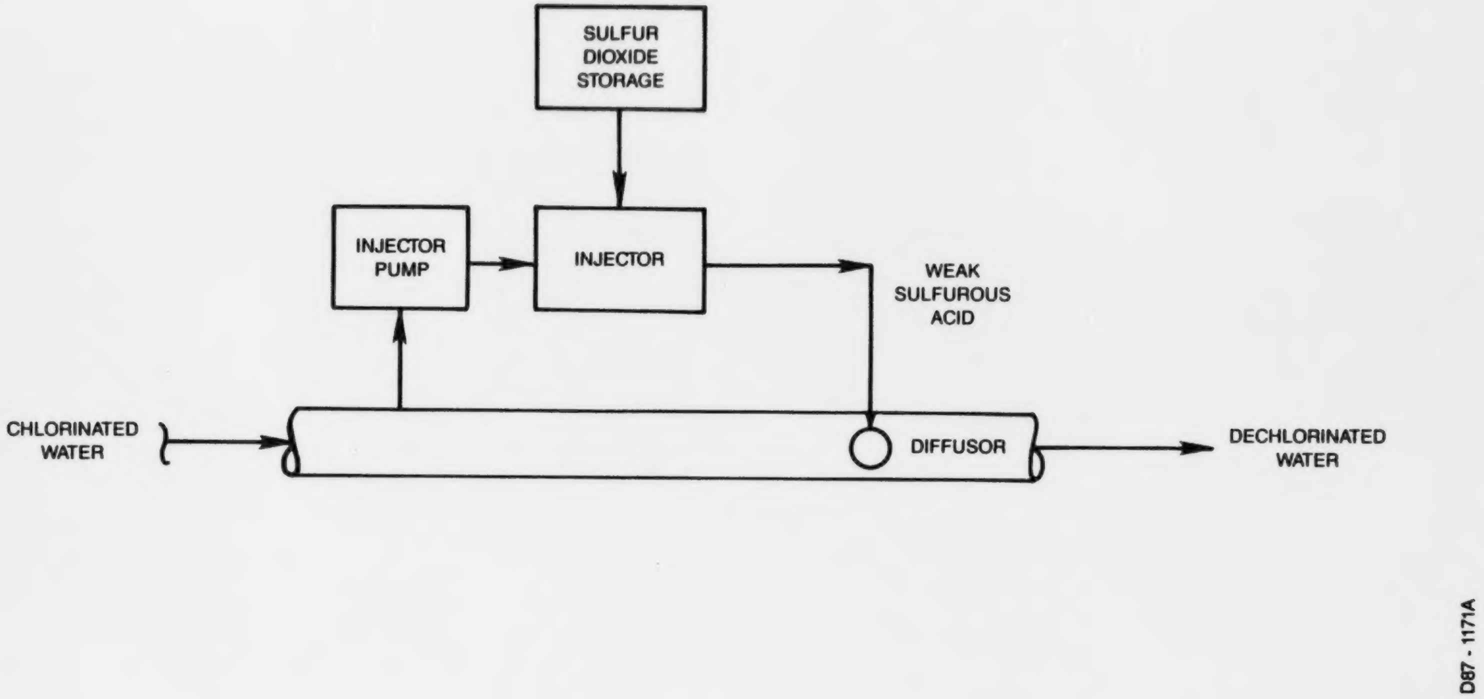

SULFUR
DIOXIDE
STORAGE
INJECTOR
PUMP
INJECTOR
WEAK
SULFUROUS
ACID
CHLORINATED
WATER
DIFFUSOR
DECHLORINATED
WATER
D87 - 1171A

Figure 3-6. Conceptual diagram of water dechlorination with sulfur dioxide.

3.2.4 Water and Wastewater Treatment

Water Dechlorination (22)--

Dechlorination is a process for partially or completely removing residual chlorine from chlorinated water. Sulfur dioxide is often used as the dechlorinating agent, because it reacts with residual chlorine very quickly with little mixing, and the process is relatively simple compared to other methods for dechlorination. The process involves absorbing gaseous sulfur dioxide into water which results in the formation of sulfite ions. The sulfite ions then react with the residual chlorine reducing it to chloride.

Figure 3-6 is a flow diagram of a typical dechlorination process using sulfur dioxide. The injector prepares a weak sulfurous acid solution by contacting sulfur dioxide gas with a small water stream. The weak sulfurous acid is intimately mixed with the chlorinated water in the diffusor. No further mixing is required for dechlorination with sulfur dioxide since the reaction with the residual chlorine is virtually instantaneous. Feed forward control is the most common method of controlling the addition of sulfur dioxide. An effluent flow rate signal is combined with a residual chlorine signal to produce a control signal to the sulfur dioxide metering equipment. The sulfur dioxide injection rate will automatically increase or decrease with changes in water flow rate and/or residual chlorine.

The release hazards associated with the dechlorination process are associated with the sulfur dioxide feed and storage systems. These hazards, which are general to all sulfur dioxide processes, are discussed in Sections 3.4 and 4.

Treatment of Chromium Waste (23)--

Sulfur dioxide is often used to treat industrial waste water which contains toxic, hexavalent chromium by reducing it to the trivalent state. Following reduction, the pH of the solution is adjusted, and the trivalent chromium precipitates as the insoluble hydroxide.

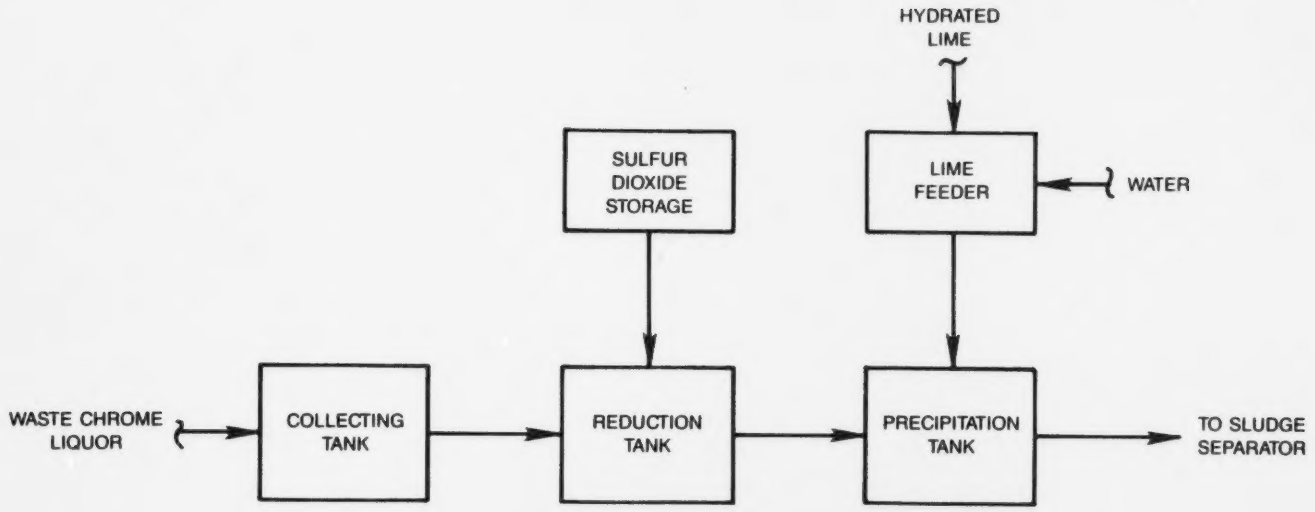

HYDRATED LIME
SULFUR DIOXIDE STORAGE
LIME FEEDER
WATER
WASTE CHROME LIQUOR
COLLECTING TANK
REDUCTION TANK
PRECIPITATION TANK
TO SLUDGE SEPARATOR
D87 - 1171A

Figure 3-7. Conceptual diagram of typical batch chromium waste treatment process.

Figure 3-7 is a flow diagram of a typical chromium reduction process. Waste liquors are collected in storage tanks and treated in a series of batches. Liquid sulfur dioxide is injected through an "L" shaped diffuser located near the bottom of the reduction tank. The reduced chrome is transferred to the liming tank and treated with sufficient hydrated lime to adjust the pH to 8.0-8.6, causing the chromium to precipitate.

As with the dechlorination process, the primary release hazards of the chrome reduction process involve the sulfur dioxide feed and storage systems. However, because the sulfur dioxide is fed as a liquid to the reduction tank, there is the additional hazard of isolating liquid sulfur dioxide between closed valves when the unit is not operational. Were this to occur, the pressure in the piping would rapidly rise as the sulfur dioxide warms, and overpressurization could result in pipe failure and an uncontrolled release of sulfur dioxide.

3.2.5 Sulfur Dioxide in the Petroleum Industry

Modified Sulfur Dioxide Extraction (24,25,26)--

Liquid sulfur dioxide is used as a solvent in the Edeleanu process in which aromatic hydrocarbons and sulfur-bearing compounds are extracted from paraffins and naphthenic hydrocarbons. A modification of the original process involves washing the extract with a washoil to further concentrate the aromatics which are often equal in value to the paraffinic raffinate.

The washoil used in the modified process is dependent on the charge. For the recovery of aromatics from naphtha fractions, a kerosine cut is used. Other washoils include a gasoil cut, such as a sulfur dioxide raffinate, for the recovery of a relatively pure aromatic stream from a petroleum fraction, or a light paraffinic hydrocarbon, such as hexane or heptane, for use with a gasoil feedstock.

Figure 3-8 is a typical flow diagram for the recovery of aromatics from a naphtha reformate. The feed is dried, deaereated, and chilled before entering

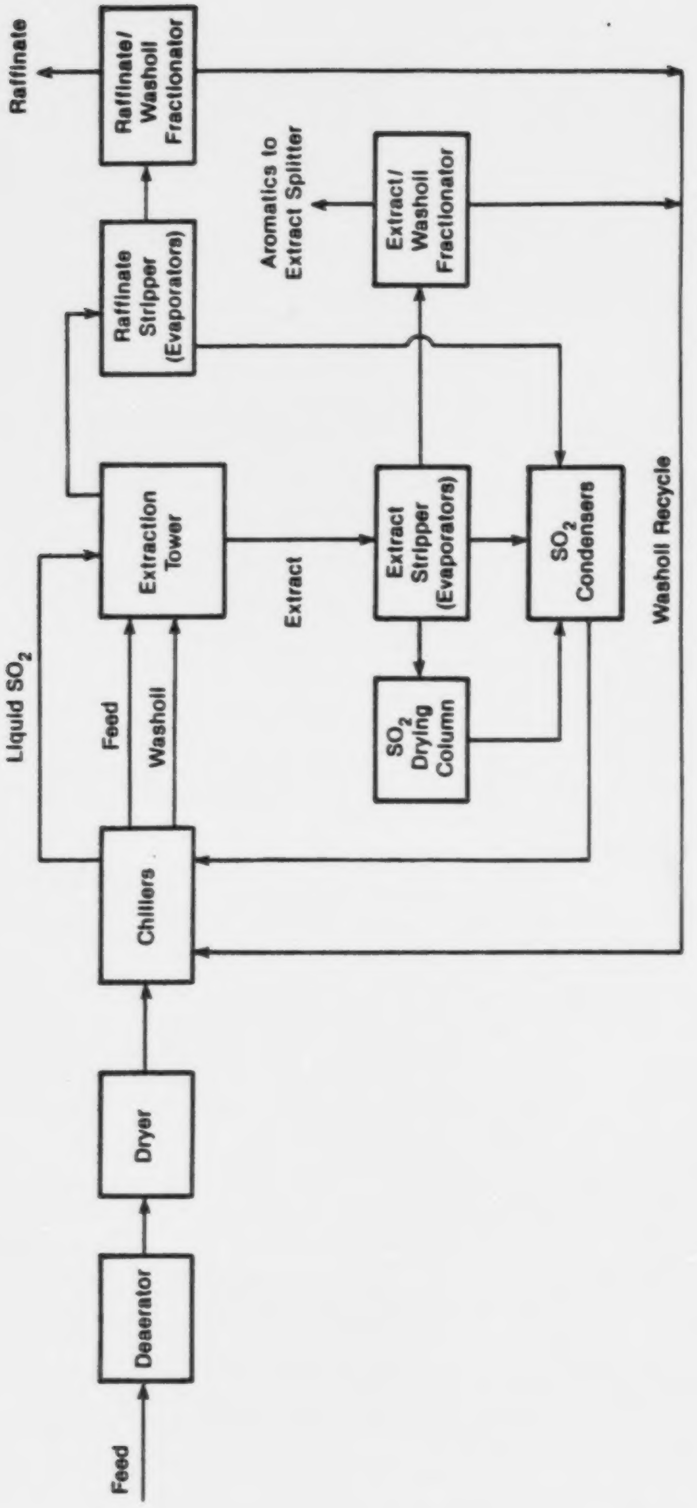

Feed
Deaerator
Dryer
Chillers
Liquid SO_2
Feed
Washoil
Extraction Tower
Raffinate Stripper (Evaporators)
Raffinate/ Washoil Fractionator
Raffinate
Extract
Extract Stripper (Evaporators)
SO_2 Drying Column
SO_2 Condensers
Extract/ Washoil Fractionator
Aromatics to Extract Splitter
Washoil Recycle
9-86-25609

Figure 3-8. Conceptual diagram of typical sulfur dioxide extraction process.

the extraction tower. Sulfur dioxide is used as the refrigerant to permit the use of common condensers, collecting equipment, and pumps for the refrigerant and the extraction solvent. The tower shown in Figure 3-8 is used for both the sulfur dioxide extraction and the stripping of the extract. The two product streams go to evaporators where the sulfur dioxide is taken overhead to be condensed in water-cooled tubular equipment. Part of the recovered sulfur dioxide is then used to cool the charge stock and the washoil to extraction temperature by flash vaporization, after which the vapor is compressed and returned to the water-cooled condensers. The water content of the circulating sulfur dioxide is controlled by sending a slip stream of vapor from the extract evaporator to a sulfur dioxide drying column. Provision is also made for removal of inert gas from the circulating sulfur dioxide.

Operating temperatures for the sulfur dioxide extraction process range from -20 °F for naphthas and kerosines to 60 °F for high-pour-point stocks (25). To maintain the sulfur dioxide as a liquid at these temperatures, required operating pressures range from less than 1 atm to 3 atm. The solvent to feed ratios range from 0.5:1 to 3:1, with the heavier charge material requiring higher solvent to oil ratios (25).

From a sulfur dioxide release perspective, a fundamental characteristic of the extraction process is the use of sulfur dioxide as a solvent rather than a reactant. Because recovery and recycle of the solvent involves a number of critical areas where sulfur dioxide is present in high concentrations or nearly pure form, the possibility for a release may be greater than what might exist in a process where it is consumed as a reactant.

High hazard areas specific to this process, excluding bulk storage and transfer (discussed in Section 3.4), include the following:

- Feed treatment to remove water from the hydrocarbon charge;
- The treating tower;
- Heat exchange equipment; and
- Sulfur dioxide drier.

Removal of water from the feed is important, because sulfur dioxide combines with water to form sulfurous acid which is corrosive to common materials of construction such as carbon steel. The feed does not contain any sulfur dioxide, but water introduced with the feed will mix with sulfur dioxide downstream. While a properly designed system should use materials which are sufficiently corrosion resistant, the materials selection will have been based on a certain feed moisture concentration. Therefore, failure of the water removal system to maintain the design moisture concentration may result in a protracted corrosion problem leading eventually to an equipment failure.

The primary concern in the treating tower is temperature control. If a process upset were to occur which resulted in a substantial temperature increase in the tower, significant expansion and vaporization of the liquid sulfur dioxide may occur resulting in a number of process problems. Furthermore, the liquid phases in the column become more miscible at higher temperatures, and a single liquid phase may result if the treating temperature is too high (26). No separation would take place in this situation, and the raffinate recovery section could become overloaded with the excess sulfur dioxide in the overhead product.

The use of sulfur dioxide as a refrigerant as well as the solvent means that it will be present in a number of heat exchange vessels in pure form. The circulating sulfur dioxide will require auxiliary equipment (pumps and compressors) as well as a considerable amount of piping in the system. A large amount of process equipment handling pure sulfur dioxide increases the chances of leaks developing in the system. Some possible causes of leaks include a loss of temperature control resulting in overpressure, corrosion, or defective or worn-out equipment. The use of water-cooled sulfur dioxide condensers also presents the possibility of a leak into the cooling water system leading to the formation of sulfurous acid and the associated corrosion hazard that this would create.

Despite precautions taken to dry the charge oil stream, small amounts of water enter the circulating sulfur dioxide stream from this source. This moisture must be continuously removed to prevent accumulation in the recycle and corrosive levels of sulfurous acid from forming. A common process used for drying the sulfur dioxide is sending a slip stream of sulfur dioxide vapor to a fractionating tower. Since a level of water collects in the reboiler, it is necessary to maintain the temperature of the reboiler sufficiently low to minimize water vaporization. The possibility of overheating the reboiler presents a potential hazard which would result in water vapor entering the sulfur dioxide stream and forming a corrosive mixture.

Liquid Sulfur Dioxide-Benzene Extraction (25)--

Two extraction processes which employ liquid sulfur dioxide as a co-solvent with benzene are the removal of low-viscosity-index constituents and the removal of wax from lube oils. These extraction processes can be advantageously arranged in series by adjusting the solvent composition. The solvent composition varies according to process requirements, ranging from 15-30% sulfur dioxide by volume for dewaxing to greater than 50% by volume for lube refining. In the dewaxing process, sulfur dioxide evaporation furnishes internal refrigeration for the precipitation of wax before its removal with closed continuous rotary filters. The extraction temperature used in the lube refining process is about 25 °F with a mixed solvent to oil ratio of about 2:1.

Process hazards associated with these two extraction processes are similar to those of the modified sulfur dioxide extraction described above. However, since the sulfur dioxide is not in pure form, the hazardous effects of this chemical resulting from a release of solvent may be less severe.

Claus Process--

The Claus process is a method of treating refinery off-gases by converting hydrogen sulfide to elemental sulfur. Although appreciable amounts of gaseous sulfur dioxide are present in the process gas stream, this stream contains an even greater concentration of hydrogen sulfide. Hence, the primary hazard in the event of a process stream release is the toxicity of the H_2S, while the adverse effects of the released sulfur dioxide would be less urgent relative to those of the released H_2S.

3.3 REPACKAGING SULFUR DIOXIDE (4,27,28)

Liquid sulfur dioxide is repackaged at several locations throughout the U.S. This process involves a number of procedures, the use of which depends on whether the transfer is from tank cars into tank trucks, or from tank cars, trucks, or other bulk storage containers into cylinders or one-ton steel drums.

When a bulk quantity of liquid sulfur dioxide arrives at a repackaging facility, filling operations may be carried out by transferring sulfur dioxide directly from the tank car or truck to the receiving container(s). However, most repackagers first transfer the sulfur dioxide to bulk storage before filling smaller containers. Tank cars and trucks are unloaded with the use of a gas compressor or transfer unit; the suction side draws gas from the top of a storage tank, while the discharge is connected to a valve on the tank car or truck which allows flow through a dip pipe terminating in the vapor phase within the tank. Thus, the liquid sulfur dioxide flows to the bulk storage vessel as the pressure in this vessel is lowered and the pressure in the tank is increased. Tank cars may alternatively be unloaded with the use of compressed air as the padding medium in the car which causes the liquid to flow into the bulk storage vessel. As tank trucks are equipped with self-powered compressors, they are always unloaded by the former procedure. The potential hazards associated with the transfer of liquid sulfur dioxide from tank cars and trucks are discussed in Section 3.4.2.

Transfer to cylinders or drums is accomplished with the use of compressed air to pad the storage vessel, causing the liquid sulfur dioxide to flow out of the vessel. The compressed air line should be equipped with a moisture and/or oil separator, followed by a drier. The dew point of the dried, compressed air should not exceed 20 °F (4). During the filling operation, the receiving vessels are mounted on scales to determine when they have been filled with the correct amount of sulfur dioxide. Some repackagers reweigh the vessels on a second scale to verify that the measurements made with the first scale were accurate.

Equipment for the refilling process usually consists of a reciprocating compressor, adapters for the cylinder and storage tank valves, and associated piping. Equipment used in repackaging operations should be constructed from materials compatible with sulfur dioxide. Suitable materials of construction for sulfur dioxide service are discussed in Section 5.

Examples of potential hazards in repackaging operations include the following:

- Equipment corrosion from sulfurous acid formed by moisture leaking into the system;

- Overpressurization of the storage vessel; and

- Overfilling of the receiving vessel.

Accidental overpressure of the storage tank could result in a release of sulfur dioxide to the atmosphere through a relief valve (if the valve is not vented to a closed system.) Overfilling could cause a release from a rupture in the piping or the receiving vessel from a pressure buildup. A latent hazard also exists in an overfilled vessel which goes undetected and leaves the repackaging facility. Other potential sources of release include leaks in the connecting piping as a result of corrosion, loose joint-pipe connections, cloggings of vapor pipes resulting in overpressure, and human error.

3.4 STORAGE AND TRANSFER

All industries which use or handle sulfur dioxide in bulk quantities must have appropriate facilities and procedures for the safe storage and transfer of this material. In this section, potential hazards associated with the storage and transfer of sulfur dioxide common to all installations are identified. Proper procedures and safety precautions for the control of these hazards for release prevention are discussed in Section 5.

3.4.1 Storage

Large quantities of liquid sulfur dioxide are stored in pressure vessels, because sulfur dioxide has a relatively low boiling point and a high vapor pressure at ambient temperatures. These vessels are generally constructed of carbon steel according to the latest edition of the American Society of Mechanical Engineers (ASME) Code for Unfired Pressure Vessels, Section VIII, Division I, and with the American National Standards Institute (ANSI) Standards for Piping and Fittings (29,30,31,32). The maximum amount of sulfur dioxide that may be stored in a container is equal to 1.25 times the water weight capacity of the container at 60 °F (2).

The primary hazard associated with the storage of liquid sulfur dioxide is failure of a pressurized storage vessel or its associated piping. There are several ways this might occur:

- Overheating;
- Overfilling; and
- Failure of safety relief devices.

A liquid-full container may result from a temperature increase of the vessel. If the vessel was overfilled to begin with, the temperature at which it will become liquid-full is lowered. Denting or other deformations of a storage container also effectively lowers the temperature at which it will become liquid-full. The maximum recommended temperature to which a vessel may be safely heated is 125 °F. Cylinders and drums are equipped with fusible safety plugs designed to melt at 165 °F to prevent rupture of the container because of overpressure, but the possibility also exists that the plug is defective and will fail to melt at the correct temperature. Furthermore, although a fusible plug will prevent a rupture of explosive force, a melted plug will still allow a complete release of the contents of the container. Larger storage vessels are generally equipped with pressure relief valves which discharge to a pressure relief vessel or vent gas scrubber.

A potential hazard exists if sulfur dioxide is stored in an area which is located near flammable or incompatible materials, especially if the area is congested or not well ventilated. Cylinders or other storage vessels kept in an area in which they are exposed to direct sunlight are also susceptible to overheating. Storage vessels in constant contact with dampness or standing water are susceptible to corrosion with the consequent development of leaks. Since the density of sulfur dioxide vapor is greater than that of air, sub-surface storage of this material is potentially hazardous, because leaking vapor will remain close to the ground and will not be readily dispersed in the atmosphere.

3.4.2 Transfer from Tank Cars and Trucks

Shipments of liquid sulfur dioxide are made in tank cars, tank trucks, 2,000-pound drums, and 150-pound cylinders. Tank cars are lagged with insulation to minimize variations in pressure with ambient temperature, and they are equipped with spring-loaded pressure-relief valves which are set to discharge at 225 psig (4). Purchasers of tank-car quantities are required to have adequate storage facilities to allow the prompt transfer of the sulfur dioxide upon arrival.

Appropriate procedures must be followed when transferring sulfur dioxide from tank cars and trucks to storage vessels to reduce the risk of a hazardous chemical release. Tank cars are unloaded by one of the two methods described in Section 3.3. (One method involves the use of a gas compressor, and the other uses compressed air as a padding medium in the tank.) Tank trucks are unloaded with the use of a self-powered compressor. Examples of potential hazards associated with the unloading of tank cars and trucks include the following:

- The pressure in the tank car or truck attains the pressure setting of its relief valve, and sulfur dioxide vapor is vented to the atmosphere;

- Moisture enters the system with the compressed air, because the pre-drying system is not functioning at design conditions, resulting in the formation of sulfurous acid which is highly corrosive to the tank car, transfer lines, and storage tank;

- Leakage resulting from pipe corrosion or loose joint-pipe connections; and

- Human error.

3.4.3 Transfer from Storage Vessels

Another aspect of the transfer of liquid or vapor sulfur dioxide to consider is the discharge of sulfur dioxide from a storage container for its designated use in the plant. This is generally accomplished by creating a pressure differential between the container and the receiving vessel or process to which it is flowing.

Cylinders and Drums--

At room temperature, a 150 lb cylinder or one-ton drum will discharge sulfur dioxide liquid at a rate of about 5 lbs per minute or vapor at a rate of 0.4 lb per minute against a discharge pressure of 10 psig (4). When higher rates are desired, the cylinder may be warmed to promote discharge of gaseous or liquid sulfur dioxide. There are several safe methods of heating the cylinder or drum including the use of a blanket type heater or electric strip, which may be controlled with a thermostat, or use of a warm bath or heated room not exceeding 125 °F. A potential hazard exists if an improper method of heating a cylinder or drum is employed, such as using a blow torch or flame, because of the danger of local overheating which may draw the temper of the steel or cause the fusible plug to melt thereby releasing the contents of the cylinder. Small, well-insulated wooden structures may be constructed in which one or two drums are heated with careful temperature control, but care must be taken to protect the fusible plugs from overheating from exposure to radiant heat.

It is possible that the evaporation of sulfur dioxide in a drum during discharge will cause the contents of the drum to be refrigerated to a point where there is little or no flow of gas. To avoid such a condition from developing, drums are often manifolded together in parallel to increase the total withdrawal rate while reducing the withdrawal rate from individual drums. A potential hazard exists in such an arrangement if there is a gaseous transfer between drums at different temperatures with subsequent reliquefaction. If this should happen, the normal filling ratio of a drum may be exceeded because of an increase in the ambient temperature. This condition could result in distortion or rupture of the drum with a consequent hazardous release of sulfur dioxide.

Another method of achieving higher flowrates of gaseous sulfur dioxide is rapidly withdrawing and vaporizing liquid sulfur dioxide in a steam or electrically heated vaporizer. A potential hazard of this process is an improper piping arrangement which allows more than one drum to be connected to the evaporator at a time. Transfer of liquid sulfur dioxide between two drums connected in parallel at even slightly different temperatures takes place rapidly and will not cease until the cooler drum is completely filled. The hazard potential is heightened if reliance is placed on manually operated isolation valves alone.

The use of nitrogen or air padding to promote the flow of sulfur dioxide from cylinders or drums is also potentially hazardous, as dangerous pressures may develop as a result of an increase in the ambient temperature, and moisture or other forms of contamination may be introduced with the gas.

Other example potential hazards include:

- The possibility of hazardous backflow into the cylinder or into the upper valve chambers when the feed valve is shut off at the drum;
- Contamination by moisture which could lead to a build-up of hydrogen pressure in closed equipment and cause an explosion of equipment with violent force;
- The possibility of isolating liquid sulfur dioxide in piping between closed valves which could lead to bursting of the line from a build-up in hydrostatic pressure; and
- The possible failure of piping connections from corrosion, improper materials of construction, or work hardening or fatigue.

Bulk Storage Containers--

Potential hazards associated with the transfer of sulfur dioxide from bulk storage containers include most of those already mentioned for cylinders and drums. The primary possibilities are overpressure as a result of overheating, corrosion from exposure to moisture or from moisture entering the piping system, isolation of liquid sulfur dioxide between closed valves, and failure to follow proper operating and maintenance procedures.

3.4.4 Transporting Sulfur Dioxide Storage Containers

Unloading containers of sulfur dioxide from a delivery vehicle or moving them within the plant is another aspect of the storage and transfer of this material. In general, potential hazards associated with the transport of sulfur dioxide within a closed vessel arise from failure to follow the proper operating procedures. Prevention of a hazardous release resulting from human error is discussed in Section 5.

SECTION 4
POTENTIAL CAUSES OF RELEASES

The potential for a hazardous release of liquid or gaseous sulfur dioxide exists in any type of chemical plant which handles this material. The possible sources of such a release are numerous. Large-scale releases may result from leaks or ruptures of large storage vessels (including tank cars on-site) or failure of process machinery (e.g., pumps or compressors) which maintain a large throughput of sulfur dioxide gas or liquid. Smaller releases may occur as a result of ruptured lines, broken gauge glasses, or leaking valves, fittings, flanges, valve packing, or gaskets.

The properties of sulfur dioxide which can promote equipment failure are a high coefficient of expansion and the corrosiveness of sulfurous acid which is formed when dry sulfur dioxide comes into contact with moisture.

In Section 3, specific release hazards associated with the manufacture, consumption, and storage of sulfur dioxide were identified. In addition to those discussed, there are also numerous general hazards which, if realized, could lead to an accidental release. Both the specific and general hazards in sulfur dioxide facilities may be broadly classified as having process, equipment, or operational causes. This classification is for convenience only. Causes discussed below are intended to be illustrative, not exhaustive. More detailed discussions of possible causes of accidental releases are planned for other parts of the prevention reference manual series.

4.1 PROCESS CAUSES

Process causes are related to the fundamentals of process chemistry, control, and general operation. Example process causes of a sulfur dioxide release include:

- Excess sulfur dioxide feed to a chlorine dioxide reactor leading to excessive exothermic reaction, combined with failure of the cooling system;

- Backflow of process reactants to a sulfur dioxide feed tank resulting in the formation of corrosive sulfurous acid or explosive reactions with incompatible materials;

- Inadequate water removal from hydrocarbon feeds in a sulfur dioxide extraction process over a long period of time leading to progressive corrosion;

- Excess feeds in any part of a process leading to overfilling or overpressuring equipment;

- Loss of condenser cooling to distillation units; and

- Overpressure in sulfur dioxide storage vessels from overheating or overfilling.

4.2 EQUIPMENT CAUSES

Equipment causes of accidental releases result from hardware failures. Some possible causes include:

- Excessive stress on materials of construction owing to improper fabrication, construction, or installation;

- Failure of vessels at normal operating conditions as a result of weakening of equipment from excessive external loadings or thermal cycling;

- Mechanical fatigue and/or shock in any equipment (mechanical fatigue could result from age, vibration, or stress cycling, for example; shock could occur from collisions with moving equipment such as cranes or other equipment in process or storage areas);

- Thermal fatigue and/or shock in reaction vessels, heat exchangers, and distillation columns;

- Brittle fracture in any equipment, especially in carbon steel equipment subjected to extensive corrosion where hydrogen embrittlement may have occurred (equipment constructed of high alloys, especially high strength alloys selected to reduce the weight of major process equipment, might be especially sensitive where some corrosion has occurred or severe operating conditions are encountered);

- Creep failure in high temperature equipment subjected to extreme operational upsets, especially excess temperatures (this can occur in equipment subjected to a fire that may have caused damage before being brought under control); and

- All forms of corrosion, including external corrosion from fugitive emissions of sulfur dioxide, pipe connections which have slowly corroded as a result of moisture entering the tubing when cylinders are switched, and stress corrosion cracking.

4.3 OPERATIONAL CAUSES

Operational causes of accidental releases are a result of incorrect procedures or human errors. Examples of these causes include the following:

- Overfilled storage vessels;
- Improper process control system operation;
- Errors in loading and unloading operations;
- Poor quality control resulting in replacement parts which do not meet system specifications;
- Inadequate maintenance in general, but especially on water removal unit operations, pressure relief systems, and other preventive and protective systems; and
- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening.

SECTION 5

HAZARD PREVENTION AND CONTROL

5.1 GENERAL CONSIDERATIONS

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where sulfur dioxide is stored and used. When developing a thorough release prevention and control plan, considerations must be made in the following areas:

- Process design,
- Physical plant design,
- Protective systems, and
- Operating and maintenance practices.

Hazards prevention and control first involves identification of specific factors in each of these areas which could directly or indirectly cause a hazardous release of sulfur dioxide. A number of these factors or potential causes of release were discussed in Sections 3 and 4. Equipment and procedures should then be examined to ensure that they are in accordance with applicable codes, standards, and regulations as a minimum. Further evaluations should then be made to determine where extra protection against a release is appropriate so that stricter equipment and procedural specifications may be developed.

The following subsections discuss specific measures for hazards prevention and control in chemical plants which maintain a significant inventory of sulfur dioxide; more detailed discussions may be found in a manual on control technologies, part of this manual series.

5.2 PROCESS DESIGN

Process design considerations involve the fundamental characteristics of the processes which use sulfur dioxide. These include the basic chemistry involved and how this chemistry is affected by the variables of flow, pressure, temperature, and composition. These characteristics are the basis for the overall process design which includes the sequence of unit operations along with equipment selection (process equipment, measuring systems, mixing systems, instrumentation, emergency equipment, etc.)

Of primary concern in process design is determining how deviations from expected conditions might initiate a series of events that could result in an accidental release. A sensitivity analysis for the purpose of assessing the potential hazards of a given design may result in process modifications which would enhance the integrity of the system. Changes may involve any aspect of the process. Possibilities include changes in the quantities of materials used, the pressure and temperature conditions, the type and sequence of unit operations, control strategies, and instrumentation.

In the context of the processes discussed in Section 3, primary consideration should be given to the items listed in Table 5-1. For each item, the specific process or unit operation for which the item is of greatest concern is given. This list is not intended to be comprehensive, and there is no guarantee that proper attention to these considerations will ensure a safe system. However, awareness and control of these items are necessary if a safe system is to be achieved.

The process upsets which are the most potentially hazardous with respect to releases of sulfur dioxide from the processes discussed in Section 3 are overheating and/or overpressuring and the leakage of moisture into the system.

TABLE 5-1. EXAMPLE PROCESS DESIGN CONSIDERATIONS FOR PROCESSES INVOLVING SULFUR DIOXIDE

Process Design Consideration	Process or Unit Operation
Contamination with water	All
Flow control of sulfur dioxide feed	All
Temperature sensing and heating media flow control	Distillation and stripping column reboilers
Temperature sensing and cooling medium flow control	Chlorine dioxide and sulfonation reactors, distillation and stripping column condensers
Adequate pressure relief	Storage tanks, reactors, distillation and stripping columns, heat exchangers
Corrosion monitoring	All, but especially recycle circuits
Temperature monitoring	Chlorine dioxide and sulfonation reactors, distillation and stripping column reboilers
Level sensing and control	Storage tanks, liquid extraction columns, reboilers and condensers

Overheating is hazardous, because it may lead to overpressure which weakens process equipment and adds to the potential for leaks at joints and valves. Wide temperature fluctuations also significantly decrease the lifespan of many materials of construction. Overpressure may occur without overheating if flowrate control is not maintained of both gas and liquid streams. Careful monitoring of the moisture content is important to prevent corrosive levels of sulfurous acid from forming. This includes regular inspection of moisture removal equipment along with measuring the moisture content of process streams and monitoring the pH of cooling water used in the process.

5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as location of systems and equipment must all be considered. The following subsections cover various aspects of physical plant design beginning with a discussion about materials of construction.

5.3.1 Equipment

Materials of Construction (1,4,33)--

Most common materials of construction are resistant to commercial dry liquid sulfur dioxide, dry sulfur dioxide gas, and hot sulfur dioxide gas containing water above its dew point. These include cast iron, carbon steel, copper, brass, and aluminum. However, wet sulfur dioxide gas, sulfurous acid, and sulfite solutions are all corrosive to many metals including iron, steel, nickel, copper-nickel alloys, and nickel-chromium-iron alloys, which are otherwise satisfactory for dry or hot sulfur dioxide service. Other suitable materials for most sulfur dioxide service are carbon, graphite, and impregnated carbon. Lead is also resistant to sulfur dioxide and sulfites under most conditions. Zinc, however, may not be used for sulfur dioxide service, because it is readily oxidized to ZnS_2O_4. Table 5-2 is a list of construction

TABLE 5-2. MATERIALS OF CONSTRUCTION FOR SULFUR DIOXIDE SERVICE (4,33)

Material	For Wet* or Dry SO_2	For Dry SO_2 Only
Admirality, Antimonial		x
Aluminum		x
Brass		x
Bronze, Commercial		x
Bronze, Olympic, Type A		x
Bronze, Olympic, Type B		x
Bronze, Telnic		x
Chlorimet 2		x
Chlorimet 3		x
Copper		x
Copper, Tellurium		x
Cupro - Nickel, 30%		x
Durco D-10		x
Durimet - 1		x
Hastelloy C		x
Haveg	x	
Haynes Stellite 1		x
Lead	x	
Steel, mild		x
Stainless Steel, Type 316	x	
Stainless Steel, Alloy 20	x	
Teflon	x	

*SO_2 containing over 1000 ppm of water

materials which have been tested and proven suitable for sulfur dioxide service (4,33).

The temperature resistance of a material must be taken into account for use with hot sulfur dioxide gas or solutions, especially if plastics or resins are used. Materials such as ceramic, glass, and stone should also be evaluated for their ability to withstand thermal shock. These latter materials are suitable for use with wet gas, sulfurous acid, or sulfite solutions.

The metals which are best suited for a wide variety of wet, dry, and hot sulfur dioxide, sulfurous acid, and sulfite service include nickel-chromium alloys such as Worthite and Durimet 20, and several of the austenitic stainless steels. While type 304 stainless steel may be satisfactory for mild conditions, types 316 and 317 are usually required for high temperatures or other severe applications. In processes which also involve the presence of sulfuric acid, the use of a 20-grade stainless steel may be warranted. Inconel is another material which is especially resistant to very hot sulfur dioxide gas.

Corrosion is a very serious hazard, and it is important to use appropriate materials for applications which may involve some exposure of the sulfur dioxide to small amounts of moisture. At approximately 300 ppm moisture, liquid sulfur dioxide discolors iron, copper, and brass. As the moisture content increases, light scale is produced at approximately 0.1 wt%, with serious corrosion occurring at 0.2 wt% and higher. For low moisture contents or where some corrosion can be tolerated, copper or brass can be used. The use of wooden tanks is common for the preparation, handling, and storage of sulfurous acid, while sulfite pulp digesters are commonly made of steel lined with acid-resistant brick. Organic coatings may be used to protect metals from corrosion unless gas diffusion through the organic film is appreciable. Organic materials used for sulfur dioxide and sulfurous acid service include hard rubber at moderate temperatures and butyl rubber which performs similarly.

For all processes involving the use of sulfur dioxide or other hazardous materials, special care should be taken to ensure that all replacement parts or new equipment are made of materials which are compatible with the chemicals involved in the process. Materials of construction suitable for specific pieces of equipment will be discussed in the following subsections which address the equipment used in sulfur dioxide storage and processing.

Storage Vessels--

Storage vessels for sulfur dioxide range in size from 150-pound cylinders to multi-ton tanks. As stated in Section 3.4.1, these containers are generally constructed of carbon steel according to the ASME Code for Unfired Pressure Vessels, Section VIII, Division I (29). The vessels are also typically constructed with provisions for keeping process solutions and gases out of the tank. The maximum allowable weight of sulfur dioxide which may be stored is 1.25 times the water weight capacity of the container measured at 60 °F (2). This quantity is expressed as a percent of the maximum volume of the container for various temperatures in Table 5-3 (4).

A large inventory of sulfur dioxide contained in storage vessels on site represents one of the most hazardous components of a chemical plant which uses this material. The most probable causes of a hazardous release from a storage vessel include overpressurization from a temperature increase and/or accidental overfilling, and corrosion resulting from contaminants entering the storage system or associated piping. This section discusses the protection devices and safety procedures associated with the storage of sulfur dioxide which are designed for the prevention of a hazardous release of this material.

Several methods for preventing overpressurization of sulfur dioxide storage vessels are employed depending on the size of the container. Cylinders and one-ton drums are manufactured with one or more fusible safety plugs which are designed to melt at a temperature of 165 °F. This safeguard, while preventing the container from a potentially explosive rupture, will still result in the complete release of the sulfur dioxide if a plug becomes hot

TABLE 5-3. MAXIMUM SAFE VOLUME OF LIQUID SULFUR DIOXIDE IN A STORAGE TANK AT VARIOUS TEMPERATURES (4)

Temperature of Liquid Sulfur Dioxide in Tank °F	Maximum Safe Volume Liquid Sulfur Dioxide in % of Full Volume at 125% Filling Density
30	86
40	87
50	88
60	89
70	90
80	91
90	92
100	93

enough to melt. For this reason, it is important to never allow the temperature of cylinders or drums to exceed 125 °F or to expose the fusible plugs to a source of radiant heat.

Larger storage vessels are generally equipped with a pressure relief valve which is protected by one or more rupture disks. These valves allow a controlled release of overpressurized contents. To prevent releases of sulfur dioxide to the atmosphere when a vessel is overpressured, the relief valve may discharge to an overflow tank in a closed system which in turn is relief vented to a scrubber system. To accommodate flashing liquid, relief piping must be sized for adequate flow. Tank cars and trucks are equipped with spring-loaded pressure relief valves which are tested to be vapor tight at 180 psig and set to discharge at 225 psig (4). For large containers, including tank cars, it may be feasible to construct a sealable housing around the container which would be vented to a scrubber system.

Overfilling of storage vessels may occur during sulfur dioxide transfer as a result of a malfunctioning measuring device, operator error, or the use of a damaged container with a reduced filling capacity which has gone unnoticed. The immediate danger of overfilling during transfer operations is an unexpected overflow and release of liquid or gaseous sulfur dioxide. The latent hazard is overpressurization and possible rupture of the container with an increase in temperature, because the temperature at which it will become liquid-full is lower than it should be.

If it is possible for a vessel to be overfilled, it should be fitted with a relief device which discharges to an overflow tank or other suitable receiver. To reduce the risk of overfilling during transfer, the storage vessel may be mounted on a scale which will indicate the weight of fluid in the container at all times. All storage vessels should also be equipped with a liquid level gauging device. The Compressed Gas Association makes the following recommendations for the design and use of these gauges (2):

- The gauge should be designed to permit reading the liquid level within plus or minus 1% of the capacity of the tank from full tank level down to at least 20% below full tank. (Readings below this level may be useful for other purposes but are not required to avoid overfilling.)

- Certain precautions must be observed if gauge glasses are used as liquid level devices. They should be protected by solid, transparent shields and guards. Gauge cocks should be provided with ball checks which will shut off the flow if the glass accidentally breaks. The ball checks will also allow the gauge cock to remain open at all times which minimizes the possibility that the glass will break by liquid expansion. The gauge should be located such that the glass and its contents do not differ greatly in temperature from the container and the sulfur dioxide inside.

- Gauges should be situated to allow ready determination of the maximum level to which the container may be filled. It is recommended that the information in Table 5-2 be attached to the tank near the gauge.

- Gauging devices which require bleeding of sulfur dioxide to the atmosphere, such as a rotary tube, fixed tube or slip tube, should be designed so that the bleed valve maximum opening is no greater than a No. 54 drill size, unless provided with an excess flow valve.

- Gauging devices should be designed for a working pressure of at least 200 pounds gauge.

A short, vented dip pipe can provide protection from overfilling in the event of failure of the volume or weight measuring device. However, this device will not always prevent an overflow of sulfur dioxide liquid. Furthermore, it will only work if there is no other outlet from the vapor space and if the line to the vent system has enough capacity.

In addition to venting provisions, storage vessels should have valve arrangements which allow the vessel to be isolated from the process to which the sulfur dioxide is being fed. Backflow of material into the upper valve chambers when the feed valve is shut off at the storage tank must be prevented because of the possibility of a corrosive solution of sulfurous acid being formed. This may be accomplished with a vented feed line or a barometric leg. Moisture must also be excluded from the storage system to prevent corrosion by sulfurous acid. For this reason, storage containers should not be in contact with standing water or exposed to continual dampness. These conditions must also be avoided to prevent external rusting of the vessel.

Process and Reaction Vessels--

General considerations for hazard control for storage vessels also apply to the design and use of process and reaction vessels. In the latter type of vessels, however, there is a greater degree of risk, as these containers are often exposed to more severe conditions of temperature and/or pressure than a regular storage vessel.

Primary considerations for process and reaction vessels include:

- Materials of construction,
- Pressure relief devices,
- Temperature control,
- Overflow protection (including high-level alarms), and
- Foundations and supports.

The foundations and supports for vessels are important design considerations, especially for large storage vessels and tall equipment such as distillation columns. The choice of construction materials is also an important consideration particularly where low-temperature conditions are encountered.

If cooling to a condenser is lost, overpressure may occur. Thus, it is necessary to use pressure relief valves to protect against leaks and ruptures which can result from overpressure. Relief protection is also necessary in the event of a fire to protect from overpressure.

Distillation and stripping columns present significant release hazards, because they contain large amounts of sulfur dioxide in pure form and have a heat input. As they are often located outdoors, external factors such as ambient temperature fluctuations and wind loadings must be properly accounted for in their design and construction, especially for the support structure.

Piping--

Schedule 80 steel pipe, butt welded and/or flanged with butt welded and/or flanged fittings, is normally used to transport pure, dry sulfur dioxide, since dry sulfur dioxide is virtually non-corrosive (4). Flanges can be slip-on and flat face and should be fitted carefully to prevent leaks. Flanges used for connecting a storage tank and the valves adjacent to it should be especially well fitted, because a leak before the first valve would necessitate unloading the tank for repair.

Because of the corrosive nature of sulfurous acid, sulfur dioxide containing moisture should be transported with 316 SS piping or other example materials listed in Table 5-2. Zinc-coated pipe should not be used, because sulfur dioxide readily oxidizes zinc in the presence of very small quantities of water.

Flexible pipe, tubing or hose is usually required somewhere in a sulfur dioxide piping system, such as when connecting to a cylinder. A commonly used material is 500 psig copper tubing with a standard yoke and adapter at the cylinder end, or a series of reverse bends may be put into the line. Since copper is prone to work hardening, the connection should be inspected each time the cylinder is changed and replaced as necessary. When making connections to a cylinder, a new 3% antimony lead or graphitized gasket should be used (34). Flexible pipe or hose should never be used where straight piping is adequate, because it does not have comparable physical strength and can fail more easily. Where a flexible connection is required, flexible metal hose designed for service with corrosive acids under pressure provides an extra measure of safety if used for carrying undiluted sulfur dioxide.

Piping connections to a tank car during transfer may be constructed out of steel, brass, copper, or stainless steel, but never out of galvanized material (4). A one-inch air line should be connected to the "GAS" valve on the tank car with a pressure gauge installed near the car. A two-inch liquid unloading line is usually sufficient (4). Ordinary ground joint or flanged unions can be used in making the various connections.

Special material considerations may be required for high or low temperature applications or other unusual or severe conditions.

Because liquid sulfur dioxide expands with temperature, bursting of lines due to hydrostatic pressure must be prevented. This may be accomplished with expansion chambers which should be located at the highest point of each section that may be closed, trapping liquid sulfur dioxide. Construction of these chambers should be in accordance with the ASME Code for Unfired Pressure Vessels, Section VIII (29). The size of the vapor chamber should provide approximately 20% excess volume for expansion (4).

The following is a list of general guidelines for the safe transport of sulfur dioxide in piping systems:

- All pipes, valves, and instrumentation should be installed and maintained in a dry, greaseless condition.

- Piping systems should have as simple a design as possible with a minimum number of joints and connections.

- A pressure reducing regulator should be installed when connecting to lower pressure piping or systems from storage vessels.

- In addition to being securely supported, pipes should be sloped with drainage provisions at the low points.

- Clips or hangers should not fit too tightly to allow for thermal expansion of the pipe.

- Piping should be protected from exposure to fire and high temperatures.

- Pressure testing should be done with dry, oil-free air; hydraulic testing must not be used because of the difficulties of drying out the system after the test is completed.

- Pipelines should always be emptied when sulfur dioxide flow is not required to prevent the possible isolation of liquid sulfur dioxide between closed valves.

Valves (35)--

Under normal conditions of flow, ball, gate or plug valves constructed of Type 316 stainless steel are used for sulfur dioxide service. In the case of gate valves, the use of the rising stem type will prevent rotation of the stem on the valve seat. Teflon packing should be used for the seats of ball or gate valves, and diaphragm valves should have teflon-faced diaphragms.

Valves in sulfur dioxide service must be carefully selected in certain circumstances. For service where water may mix with the sulfur dioxide in contact with the valve it must be corrosion resistant. Valves for such service may be constructed of or lined with materials listed in Table 5-2. Diaphragm valves with inner lining of the diaphragm constructed of type 316 stainless steel are suitable for service under corrosive conditions. For more severe conditions valves should be constructed of "20-alloys" which minimize the tendency of a valve to "freeze". Teflon packing is suitable for wet or dry sulfur dioxide service.

Check valves must be installed in the line between the sulfur dioxide feed vessel and the process to prevent hazardous backflow into the sulfur dioxide feed line when the shutoff valve is closed, or when the container supplying sulfur dioxide is empty. It is important to keep sulfur dioxide from mixing with moisture in closed equipment, because hydrogen pressure may be generated leading to an explosion with violent force. A swing check valve made of type 316 stainless steel, or Alloy 20 for longer life, should be used.

A needle valve is often used for accurate flow control at low flow rates. For high flow rates, a globe valve with V-ports should be used. These should also be constructed of type 316 stainless steel, or Alloy 20 for longer life. Gate valves are better than globe valves for use as a shutoff valve because of the lower pressure drop in a gate valve.

Excess flow valves should be considered for sulfur dioxide in vessels, tank cars, and other places where unintentional high liquid discharge rates need to be prevented. In the event that a liquid discharge line is broken, the resulting high flow rate would cause the valve to close off, restricting the escape of sulfur dioxide.

Process Machinery--

Process machinery refers to rotating or reciprocating equipment that may be used in the transfer or processing of sulfur dioxide. Included in this classification are pumps and compressors which may be used to move liquid or gaseous sulfur dioxide where gas pressure padding is insufficient or inappropriate.

Pumps--Many of the considerations for sulfur dioxide piping and valves also apply to pumps. To assure that a given pump is suitable for a sulfur dioxide service application, the design engineer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Pumps should be constructed with materials which are resistant to sulfur dioxide at operating temperatures and pressures. They should be installed dry and oil-free. Lubricating oil should be resistant to breakdown as a result of contact with sulfur dioxide. Highly refined mineral oil may be suitable for many applications (36). Even with the use of special lubricants, it is important that pump design not allow sulfur dioxide or lubricating oil to enter seal chambers where they may contact one another. Net positive suction head (NPSH) considerations are especially important for sulfur dioxide, since pumping the liquid near its boiling point may be common. (Sulfur dioxide is a gas at typical ambient conditions.) The pump's supply tank should have high and low level alarms; the pump should be interlocked to shut off at low supply level or low discharge pressure. External pumps should be situated inside a diked area and should be accessible in the event of a tank leak.

In some cases, the potential for seal leakage may rule out the use of rotating shaft seals. Some pump types which either isolate the seals from the process stream or eliminate them altogether include canned-motor, vertical extended-spindle submersible, magnetically-coupled, and diaphragm (37).

Canned motor pumps are centrifugal units in which the motor housing is interconnected with the pump casing. Here, the process liquid actually serves as the bearing lubricant. An alternative concept is the vertical pump often used on storage tanks. Vertical pumps consist of a submerged impeller housing connected by an extended drive shaft to the motor. The advantages of this arrangement are that the shaft seal is above the maximum liquid level (and is therefore not made wet by the pumped liquid), and the pump is self-priming, because the liquid level is above the impeller.

Vertical pumps should be provided with double-packed seal chambers which are designed to prevent contact of sulfur dioxide and any reactive material. Seal gas should be dry, oil-free, and inert to sulfur dioxide. The seal gas pressure should be greater than tank pressure, and a seal gas backup system should be considered.

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the pumped liquid.

Centrifugal pumps often have a recycle loop back to the feed container which prevents overheating in the event that the pump is deadheaded (i.e., the discharge valves close.) Deadheading also is a concern with positive displacement pumps. To prevent rupture, positive displacement pumps commonly have a pressure relief valve which bypasses to the pump suction. Because of the probability of eventual diaphragm failure, the use of diaphragm pumps should be carefully considered in view of this hazard potential.

Pumps are not always necessary; in some circumstances, liquid sulfur dioxide is moved by pressure padding. With sulfur dioxide cylinders and ton containers, the liquid may be displaced from the vessel by the force of sulfur dioxide's vapor pressure. With other types of vessels, an inert gas such as dry nitrogen may be used to force liquid from the tank. Padding system designs reflect the operating conditions and limitations (e.g., required flow rate) and therefore must be custom designed for a process.

Compressors--Sulfur dioxide compressors include reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors. Detailed descriptions of these compressors may be found in the technical literature (37).

While it is often possible to avoid using rotary shaft seals with sulfur dioxide pumps, compressors in sulfur dioxide service usually require special seals such as double labyrinth seals. These seals have a series of interlocking touch points which, by creating many incremental pressure drops, reduce total leakage. To further reduce leakage, dry air is injected into the seal. For reciprocating compressors, a two-compartment distance piece with purge gas may be used to prevent shaft exposure to sulfur dioxide. In the event of deadheading, a compressor discharge can have a pressure relief mechanism which vents to the compressor inlet or to a scrubber system. The former appears to be satisfactory for a short-term downstream flow interruption. Where a sustained interruption might occur, relief to a scrubber system would be safer. As with pumps, compressors for sulfur dioxide service may require the use of lubricating oils that are resistant to breakdown by sulfur dioxide.

Miscellaneous Equipment--

Pressure Relief Devices--Pressure relief devices for sulfur dioxide service should be constructed in accordance with CGA S-1.3 - "Pressure Relief Device Standards - Part 3 - Compressed Gas Storage Containers" (38). All wetted parts of relief valves and rupture disks should be constructed from materials compatible with sulfur dioxide at the operating temperature and pressure. For balanced relief valves, the balance seals must also be made of a corrosion resistant material. For most applications, 316 stainless steel is an appropriate material of construction.

Fugitive emissions of sulfur dioxide can result in external corrosion of a relief valve. For this reason it may be appropriate to construct the entire relief device of a material that is resistant to wet sulfur dioxide.

Measures should be taken to ensure that process equipment is not isolated from its relief system. To provide continuous pressure relief protection when a device is out of service for maintenance, equipment may be provided with dual relief systems, each sized to provide the total required flow capacity. Piping and valves should be arranged so that one of the systems always provides protection. Stop valves installed between a vessel and its relief device should have a full port area that is at least equal to that of the pressure relief device inlet. These valves should be locked open or have handles removed when the protected vessel is in use. If the discharge is to be piped to a closed disposal system, such as a scrubber, the pressure drop caused by the additional piping must be considered and the relief device sized accordingly.

Rupture disks may be used to protect pressure relief valves from constant contact with the contents of the storage vessel. Rupture disks should not be used in sulfur dioxide service where the ruptured disk discharges directly into the atmosphere. If the disk relieves the contents of the container through a spring-loaded pressure relief valve, a small vent should be provided in the chamber between the disk and the valve to prevent any back pressure on the rupture disk. Because operating pressures exceeding 70% of a disk bursting pressure may induce premature failure, a considerable margin should be allowed when sizing rupture disks.

Instrumentation--Rotameters may be used for measuring the rate of flow of sulfur dioxide gas or liquid. If liquid sulfur dioxide is being measured through a meter in which the liquid takes a pressure drop, the sulfur dioxide liquid must be cooled well below its boiling point to prevent bubbling which will destroy the accuracy of the measurement (4). For high pressure work the glass tube should be enclosed in a vented shield or, preferably, a steel-armored type.

Instrumentation must be constructed of materials suitable for sulfur dioxide service, and special attention should be paid to materials used for wet sulfur dioxide. Thermocouples may be enclosed in glass sleeves for corrosion protection in some processes. An additional consideration for all instruments is that they should be protected from external corrosion which may be caused by fugitive emissions of sulfur dioxide or other process chemicals.

Gaskets--Gaskets should be graphited or Teflon impregnated asbestos, 1/16th-inch thick (4). Gaskets should have smooth faces. Compensation for flaws in gasket faces must not be made by the use of thicker gaskets (4).

5.3.2 Plant Siting and Layout

The siting and layout of a particular sulfur dioxide facility is a complex issue which requires careful consideration of numerous factors. These include the other processes in the area, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding.

The objective in siting and layout should be to avoid fires, explosions, releases of toxic gases and other dangerous incidents, rather than to protect people from their consequences after the fact. However, while prevention is always the first priority, complete prevention may be impossible. For this reason, siting and layout of facilities or individual equipment items should be done in a manner that reduces exposure to persons, both in and out of the plant, in the event of a release. Protection for people, control equipment, and records can be had by locating them in specially designed buildings. Siting should further provide ready access in the event of an emergency for both evacuation purposes and the use of emergency equipment. However, advantage should also be taken of barriers, either man-made or natural which could reduce the hazards of releases.

Various techniques are available for formally assessing a plant layout and should be considered when planning high hazard facilities (39).

The siting and layout of any facility handling sulfur dioxide should adhere to the following general guidelines:

- Areas in which sulfur dioxide hazards exist should have an adequate number of well marked exits through which personnel can escape quickly if necessary; doors should open outward and lead to unobstructed passageways;

- The plant is laid out so that, whenever possible, there are no confined spaces between equipment; large distances between large inventories and sensitive receptors is desirable;

- Access to platforms above ground level should be by stairway in preference to cat ladders, and work areas above ground level should have alternative means of escape;

- Large inventories of sulfur dioxide should be kept away from possible sources of fire or explosion; special consideration should be given to the location of furnaces and other permanent sources of ignition in the plant; and

- Storage facilities should be located in cool, dry, well-ventilated areas, away from heavily trafficked areas and emergency exits.

An existing facility may not be able to conform to all of these criteria. When this is true, other prevention measures must be taken to compensate for deficiencies in plant layout.

Because heat causes thermal expansion of liquid sulfur dioxide, measures should be taken to situate piping, storage vessels, and other sulfur dioxide equipment so that they are not adjacent to piping which carries flammable materials, hot process piping, equipment, steam lines, and other sources of direct or radiant heat. Storage should also be situated away from control rooms, offices, utilities, and laboratory areas.

In the event of an emergency, there should be more than one entrance to the facility which is accessible to emergency vehicles and crews. Storage vessel shutoff valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. Dikes reduce evaporation while containing the liquid. It is also possible to equip a diked area to allow drainage to an underground containment sump. This sump would be vented to a scrubber system for safe discharge. A full containment system using a specially constructed building vented to a scrubber is another possible option. This type of secondary containment could be considered for large volume, liquid sulfur dioxide storage tanks.

5.3.3 Transfer and Transport Facilities

Transfer and transport facilities where both road vehicles and rail tankers are loaded or unloaded are potential accident areas because of vehicle movement and the intermittent nature of the operations. Therefore, special attention should be given to the design of these facilities.

As mentioned in the previous section, tank car and tank truck facilities should be located away from sources of heat, fire and explosion. Before unloading, tank vehicles should be securely moored; an interlocked barrier system is commonly used. Tank cars should also be protected on both ends by derailers or on the switch end if located on a dead end siding. Sufficient space should be available to avoid congestion of vehicles or personnel during loading and unloading operations. Vehicles, especially trucks, should be able to move into and out of the area without reversing. High curbs around transfer areas and barriers around equipment should be provided to protect equipment from vehicle collisions.

Correct procedures must be followed when unloading and handling small sulfur dioxide storage vessels such as cylinders and drums. Dragging, sliding, or rolling cylinders, even for short distances, is not acceptable. Lifting magnets, slings of rope or chain, or any other device in which the cylinders themselves form a part of the carrier should never be used for transporting cylinders. Drums may be moved over short distances with the use of hooks which are connected to a chain sling or a lifting beam supported by a hoist or monorail (4). It is important to instruct operating personnel in the proper use of such equipment, since additional stresses are imposed on slings through angles developed, which the operators may not be aware of, thus creating an overload on the system. Suppliers' vehicles specially equipped so that drums lie in cradles cannot be safely loaded or unloaded with conventional fork lift trucks. A system of runway beams in the drum storage area is the preferred method.

5.4 PROTECTION TECHNOLOGIES

This subsection describes two types of protection technologies for containment and neutralization. These are:

- Enclosures, and
- Scrubbers.

More detailed discussions on these systems are planned for other parts of the prevention reference manual series.

5.4.1 Enclosures

Enclosures refer to containment structures which capture any sulfur dioxide spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment and discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to scrubbers for neutralization.

Specially designed enclosures for sulfur dioxide storage or process equipment do not appear to be in widespread use. The principle that it may be preferable to locate toxic operations in the open air has been mentioned in the literature (39), along with the opposing idea that sometimes enclosure may be appropriate. The desirability of enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations within enclosed areas. However, if the issue is providing for secondary containment, total enclosure may be appropriate.

If an enclosure is deemed appropriate for a given installation, it should be equipped with continuous monitoring equipment and adequate fire protection. Alarms should sound whenever lethal or flammable concentrations are detected.

Care must be taken when an enclosure is built around pressurized equipment. From an economic standpoint, it would not be practical to design an enclosure to withstand the pressures associated with the sudden failure of a pressurized vessel. Therefore, if an enclosure is built around pressurized equipment, it should be equipped with some type of explosion protection, such as rupture plates. These components are designed to fail at a pressure lower than the design pressure of the enclosure, thus preventing the entire structure from failing.

The type of structures that appear to be suitable for sulfur dioxide are concrete blocks, or concrete sheet buildings or bunkers. An enclosure would have a ventilation system designed to draw in air when it is vented to a scrubber or the atmosphere. The bottom section of an enclosure which is used for stationary storage containers should be liquid tight to retain any liquid sulfur dioxide that might be spilled. Enclosures around rail tank cars which are used for storage do not normally lend themselves easily to effective liquid containment. However, containment can be accomplished if the floor of the enclosure is excavated several feet below the track level while the tracks are supported at grade in the center.

While the use of enclosures for secondary containment of sulfur dioxide spills or releases is not known to be widely used, it might be considered for areas near sensitive receptors.

5.4.2 Scrubbers

Scrubbers are a traditional method for absorbing toxic gases from process streams. These devices can be used for the control of sulfur dioxide releases from vents and pressure relief discharges, from process equipment, or from secondary containment enclosures.

Sulfur dioxide discharges could be contacted with an aqueous scrubbing medium in any of several types of scrubbing devices. An alkaline solution is required to achieve effective absorption, because absorption rates with water alone might require unreasonably high liquid-to-gas ratios. However, water scrubbing could be used if an alkaline solution were not available. Typical alkaline solutions for an emergency scrubber could be calcium hydroxide, derived from slaked lime, or sodium hydroxide or sodium carbonate.

Types of scrubbers that might be appropriate include spray towers, packed bed scrubbers, and venturis. Other types of special designs might be suitable, but complex internals subject to corrosion do not seem to be advisable.

Whatever type of scrubber is selected, a complete system would include the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used as protection against emergency releases, consideration must be given to how it would be activated in time to respond to an emergency load. One approach used in some process facilities is to maintain a continuous circulation of scrubbing liquor through the system. For many facilities this would not be practical, and the scrubber system might be tied into a trip system to turn it on when it is needed. However, with this system a quantity of sulfur dioxide would be released prior to actuation of the scrubber (i.e., starting up a blower and turning on the flow of liquid).

The scrubber system must be designed so as not to present excessive resistance to the flow of an emergency discharge. The pressure drop should be only a small fraction of the total pressure drop through the emergency discharge system. In general, at the liquid-to-gas ratios required for effective scrubbing, spray towers have the lowest, and venturis the highest pressure drops. While packed beds may have intermediate pressure drops at proper liquid-to-gas ratios, excessive ratios or plugging can increase the pressure drop substantially. However, packed beds have higher removal efficiencies than spray towers or venturis.

In addition, the scrubber system must be designed to handle the "shock wave" generated during the initial stages of the release. This is particularly important for packed bed scrubbers since there is a maximum pressure with which the gas can enter the packed section without damaging the scrubber internals.

Design of emergency scrubbers can follow standard techniques discussed in the literature, carefully taking into account the additional considerations just discussed. An example of the sizing of an emergency packed bed scrubber is presented in Table 5-4. This example provides some idea of the size of a typical emergency scrubber for various flow rates. This is an example only and should not be used as the basis for an actual system which might differ based on site specific requirements.

Another approach is the drowning tower where the sulfur dioxide vent is routed to the bottom of a large tank of uncirculating caustic. The drowning tower does not have the high contact efficiency of the other scrubber types, but can provide substantial capacity on demand.

TABLE 5-4. EXAMPLE OF PERFORMANCE CHARACTERISTICS FOR AN EMERGENCY PACKED BED SCRUBBER FOR SULFUR DIOXIDE

Basis: Inlet stream of 50% SO_2 in 50% air. Constant gas flow per unit cross-sectional area of 290 scfm/ft^2.

Packing: 2-inch plastic Intalox® saddles.

Pressure Drop: 0.5 inch water column

Scrubbing Medium: 8% (wt) NaOH solution

Removal Efficiency, %	50	90
Liquid to Gas Ratio (gal/thousand scf)		
-- at flooding	220	220
-- operating	130	130
Packed Height, ft.	4.6	15.3

Column Diameter and Corresponding Gas Flow Rates for Both Removal Efficiencies

Column Diameter (ft)	Flow Rate (scfm)
0.5	60
1.0	240
2.0	960
6.6	10,000

5.5 MITIGATION TECHNOLOGIES

If, in spite of all precautions, a large release of sulfur dioxide were to occur, the first priority would be to rescue workers in the immediate vicinity of the accident and evacuate persons from downwind areas. The source of the release should be determined, and the leak should be plugged to stop the flow if this is possible. This post release mitigation effort requires that the source of the release is accessible to trained plant personnel, and adequate personnel protection is readily available. Personnel protection includes such items as portable breathing air and chemically resistant protective clothing.

The next primary concern becomes reducing the consequences of the released chemical to the plant and the surrounding community. Reducing the consequences of an accidental release of a hazardous chemical is referred to as mitigation. Mitigation technologies include such measures as physical barriers, water sprays and fogs, and foams where applicable. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been spilled or released to the atmosphere in order to reduce the atmospheric concentration and the area affected by the chemical. The mitigation technology chosen for a particular chemical depends on the specific properties of the chemical including its flammability, toxicity, reactivity, and those properties which determine its dispersion characteristics in the atmosphere.

If a release occurs from a pressurized sulfur dioxide storage tank above the boiling point, a gas cloud or a quantity of liquid will immediately flash off as vapor, while the remaining liquid will be cooled to the normal boiling point of 14.0 °F. Heat transfer from the air and ground will result in further vaporization of the released liquid. Since the sulfur dioxide accidentally released from a refrigerated storage tank is already at or below its normal boiling point, a comparable quantity of vapor will not flash off, as with the pressurized release discussed above, but heat transfer from the environment will cause evaporation and the formation of a vapor cloud. It is therefore desirable to minimize the area available for heat transfer to a liquid spill which in turn will minimize the rate of evaporation. Mitigation technologies which are used to reduce the rate of evaporation of a released liquified gas include secondary containment systems such as impounding basins and dikes.

5.5.1 Secondary Containment Systems (40)

Specific types of secondary containment systems include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. The type of containment system best suited for a particular storage tank or process unit will depend on the risk associated with an accidental release from that location. The inventory of sulfur dioxide and its proximity to other portions of the plant and to the community should be considered when selecting a secondary containment system. The secondary containment system should have the ability to contain spills with a minimum of damage to the facility and its surroundings and with minimum potential for escalation of the event.

Secondary containment systems for sulfur dioxide storage facilities may consist of one of the following:

- An adequate drainage system underlying the storage vessels which terminates in an impounding basin having a capacity as large as the largest tank served; or

- A dike surrounding the storage area with a capacity as large as the largest tank served.

These measures are designed to prevent the accidental discharge of liquid sulfur dioxide from spreading to uncontrolled areas.

The most common type of containment system is a low wall dike surrounding one or more storage tanks. Generally, no more than three tanks are enclosed within one diked area to reduce risk. Dike heights usually range from three to twelve feet depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid tight and able to withstand the hydrostatic pressure and temperature of a spill. Low wall dikes may be constructed of steel, concrete, or earth. If earthen dikes are used, dike walls must be constructed and maintained to prevent leakage through the dike. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the dikes to provide additional vapor storage capacity. If there are more than one tank in the diked area, the tanks should be situated on beams above the maximum liquid level attainable in the impoundment.

A low wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. By preventing the liquid from spreading, the low wall dike can reduce the surface area of the spill. Reducing the surface area will reduce the rate of evaporation. The low wall dike will partially protect the spill from wind; this can reduce the rate of evaporation. A dike with a vapor fence will provide extra protection from wind and will be even more effective at reducing the rate of evaporation.

A low wall dike will not reduce the impact of a gaseous sulfur dioxide release. A dike also creates the potential for sulfur dioxide and trapped water to mix in the dike, which may accelerate the rate of evaporation and form highly corrosive sulfurous acid. If materials that would react violently with sulfur dioxide are stored within the same diked area then the dike will increase the potential for mixing the materials in the event of a simultaneous leak. A dike also limits access to the tank during a spill.

A remote impounding basin is well suited to storage systems where more than one tank are served and a relatively large site is available. The flow from a sulfur dioxide spill is directed to the basin by dikes and channels under the storage tanks which are designed to minimize exposure of the liquid to other tanks and surrounding facilities. Because of sulfur dioxide's high vapor pressure the trenches that lead to the remote impounding basin as well as the basin itself should be covered to reduce the rate of evaporation. Additionally, the impounding basin should be located near the tank area to minimize the amount of sulfur dioxide that evaporates as it travels to the basin.

This type of system has several advantages. The spilled liquid is removed from the immediate tank area. This allows access to the tank during the spill and reduces the probability that the spilled liquid will damage the tank, piping, electrical equipment, pumps or other equipment. In addition, the covered impoundment will reduce the rate of evaporation from the spill by protecting the spill from wind or heating from sunlight.

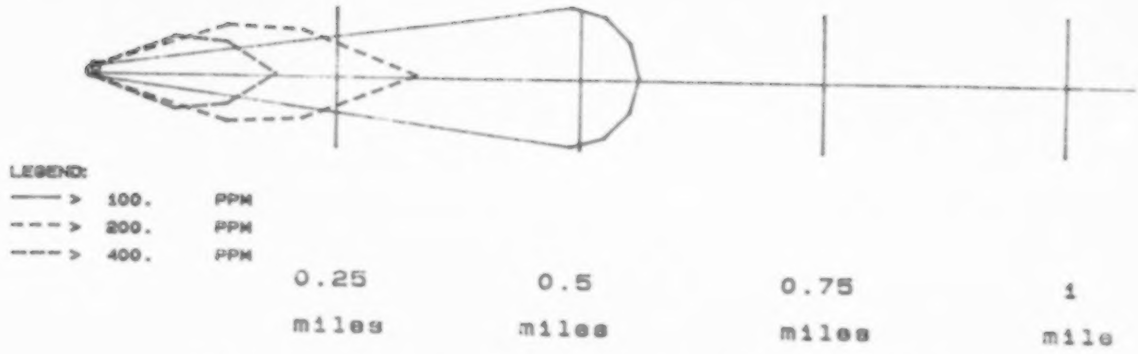
A limitation of a remote impounding basin is that there is still the potential for water or other incompatible materials to be trapped in the impoundment and mix with the incoming sulfur dioxide. Remote impounding basins do not reduce the impact of a gaseous sulfur dioxide release.

Although few authorities for sulfur dioxide facilities require them, high wall impoundments may be a good secondary containment choice for selected systems. Circumstances which may warrant their use include limited storage site area, the need to minimize vapor generation rates, and/or the tank must be protected from external hazards. Maximum vapor generation rates will generally be lower for a high wall impoundment than for low wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced with the use of insulation on the wall and floor in the annular space. High impounding walls may be constructed of low temperature steel, reinforced concrete, or prestressed concrete. A weather shield may be provided between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. For high wall impoundments, the walls may be designed with a volumetric capacity greater than that of the tank to provide vapor containment. Increasing the height of the wall also raises the elevation of any released vapor.

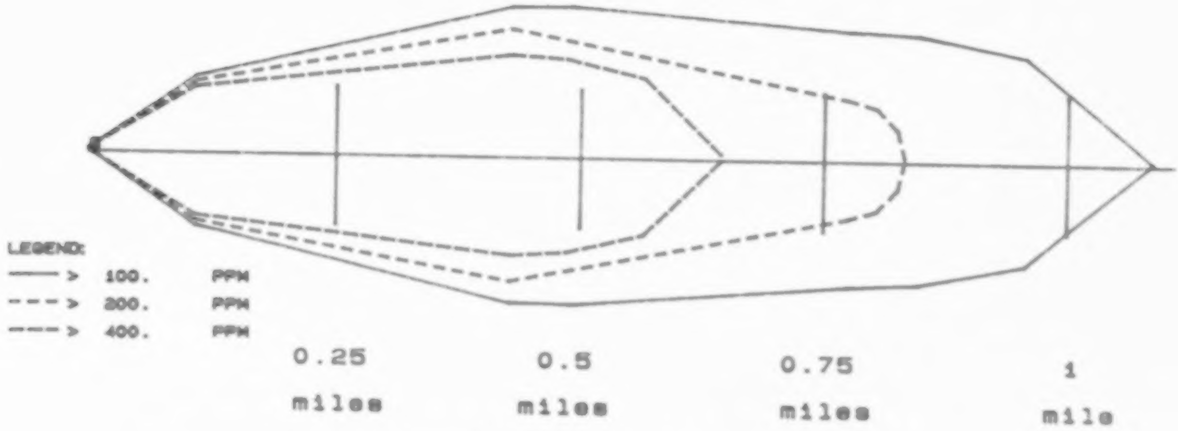
One disadvantage of these dikes is that the high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to access the tank for inspection and maintenance. As with low wall dikes, piping should be routed over the wall if possible. The closeness of the wall to the tank may necessitate placement of the pump outside of the wall, in which case the tank outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pipe penetration and pump may be provided, or a low dike may be placed around the entire wall.

An example of the effect of diking as predicted by a vapor dispersion model is shown in Figure 5-1 (41). This figure shows sulfur dioxide vapor clouds at the time when the farthest distance away from the source is exposed to concentrations above the IDLH. With diking, the model predicts that downwind distances up to 3000 feet from the source of the release could be exposed to concentrations above the IDLH. Three minutes are required for the vapors to reach the maximum down wind distance. Without diking, the model predicts that downwind distances up to 5800 feet from the source could be exposed to concentrations above the IDLH. Seven minutes are required for the vapors to reach this distance.

One further type of secondary containment system is one which is structurally integrated with the primary system and forms a vapor tight enclosure around the primary container. Many types of arrangements are possible. A double walled tank is an example of such an enclosure. These systems may be considered where protection of the primary container and containment of vapor for events not involving foundation or wall penetration failure are of greatest concern. Drawbacks of an integrated system are the greater complexity of



Release from a tank surrounded by a 25 ft. diameter dike.
Elapsed Time: 3 minutes



Release from a tank with no dike.
Elapsed Time: 7 minutes

Common Release Conditions

Storage Temperature = 85°F
Storage Pressure = 51 psig
Ambient Temperature = 85°F

Wind Speed = 10 mph
Atmospheric Stability Class = C
Quantity Released = 5000 gallons
through a 2-inch hole

Figure 5-1. Computer model simulation showing the effect of diking on the vapor cloud generated from a release of liquified sulfur dioxide.

the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Provision should be made for drainage of rainwater from diked areas. This will involve the use of sumps and separate drainage pumps, since direct drainage to stormwater sewers would presumably allow any spilled sulfur dioxide to follow the same route. Alternately, a sloped rain hood may be used over the diked area which could also serve to direct the rising vapors to a single release point (40). The ground within the enclosure should be graded to cause the spilled liquid to accumulate at one side or in one corner. This will help to minimize the area of ground to which the liquid is exposed and from which it may gain heat. In areas where it is critical to minimize vapor generation, surface insulation may be used in the diked area to further reduce heat transfer from the environment to the spilled liquid. The floor of an impoundment should be sealed with a clay blanket to prevent the sulfur dioxide from seeping into the ground; percolation into the ground causes the ground to cool more quickly, increasing the vapor generation rate. Absorption of the sulfur dioxide into water in the soil would also release additional heat.

5.5.2 Flotation Devices and Foams (42,43)

Other possible means of reducing the surface area of spilled sulfur dioxide include placing impermeable flotation devices on the surface, and applying water-based foams. Placing an impermeable flotation device over a spilled chemical is a direct approach for containing toxic vapors with nearly 100 percent efficiency. However, being able to use such devices requires acquisition in advance of a spill and storage until needed, and in all but small spills deployment may be difficult. In addition, material and dispersal equipment costs are a major deterrent to their use (42).

The use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals. Unfortunately, it is difficult to accurately quantify the benefits of foam systems, because the effects will vary as a function of the chemical spilled, foam type, spill size, and atmospheric conditions. With regard to liquefied gases, it has been found that with some materials, foams have a net positive effect, but with others, foams may exaggerate the hazard.

One approach to a sulfur dioxide spill is dilution with water. However, dilution of sulfur dioxide with water results in the formation of highly corrosive sulfurous acid. A water-based foam cover provides an alternative means of diluting the sulfur dioxide. When a foam cover is first applied, an increase in the boil off rate is generally observed which causes a short-term increase in the downwind sulfur dioxide concentration. The initial foam cover may be destroyed by violent boiling, in which case a second application is necessary. Once a continuous foam layer is formed, a net positive effect will be achieved in the downwind area. The reduction in downwind concentration is a result of both increased dilution with air, because of a reduced vaporization rate, and the increased buoyancy of the vapor cloud. This latter effect is a result of the vapor being warmed as it rises through the blanket by heat transfer from the foam and by the heat of solution of sulfur dioxide in water; the warmed vapor cloud will have greater buoyancy and will disperse in an upward direction more rapidly.

The extent of the downwind reduction in concentration will depend on the type of foam used. Research in this area has indicated that medium to high expansion foams (300 to 350:1) give significantly better results than do low expansion foams (6 to 8:1) (43). Furthermore, a high expansion foam will cause a smaller initial increase in boil off than a low expansion foam.

Regardless of the type of foam used, the slower the foam's drainage rate, the better its performance will be. A slow draining foam will spread more evenly, show more resistance to temperature and pH effects, and collapse more slowly. The initial cost for a slow draining foam may be higher than for other foams, but a cost effective system will be realized in superior performance.

5.5.3 Mitigation Techniques for Sulfur Dioxide Vapor (44,45,46)

The extent to which the escaped sulfur dioxide vapor can be removed or dispersed in a timely manner will be a function of the quantity of vapor released, the ambient conditions, and the physical characteristics of the vapor cloud. The behavior and characteristics of the sulfur dioxide cloud will be dependent on a number of factors. These include the physical state of the sulfur dioxide before its release, the location of the release, and the atmospheric and environmental conditions. Many possibilities exist concerning the shape and motion of the vapor cloud, and a number of predictive models of dispersion have been developed. As a result of the higher specific gravity of pure sulfur dioxide, large accidental releases of sulfur dioxide will often result in the formation of sulfur dioxide-air mixtures which are denser than the surrounding atmosphere. This type of vapor cloud is especially hazardous, because it will spread laterally and remain close to the ground.

One means of dispersing as well as removing toxic vapor from the air is with the use of water sprays or fogs. However, dilution of sulfur dioxide with water results in the formation of highly corrosive sulfurous acid and presents an additional health hazard to plant personnel as well as corrosion problems for machinery and equipment. In addition, to be effective, an impractically large volume of water would have to be used, although it may be beneficial in controlling relatively small releases whose principal hazard is to plant personnel (44). An alternative is to use a mild aqueous alkaline spray system which would act as a neutralizing agent for the acid.

The dispersing medium is commonly applied to the vapor cloud by means of hand-held hoses and/or stationary spray barriers. For effective absorption, it is important to direct fog or spray nozzles from a downwind direction to avoid driving the vapors downwind more quickly. Other important factors relating to the effectiveness of alkaline sprays are the distance of the nozzles from the point of release, the fog pattern, nozzle flow rate, pressure, and nozzle rotation. If the right strategy is followed, a "capture zone" can be created downwind of the release into which the sulfur dioxide vapor will drift and be absorbed. In low wind conditions, two fog nozzles should be placed upwind of the release to ensure that the sulfur dioxide cloud keeps moving downwind against the fog nozzle pressures. If an alkaline fog is used to absorb sulfur dioxide vapors from a diked area containing spilled liquid sulfur dioxide, great care must be taken not to direct alkaline solution into the liquid sulfur dioxide itself.

Spray barriers consist of a series of nozzles which can be directed either up or down. If placed directly downwind from the point of sulfur dioxide release, these barriers will absorb some of the sulfur dioxide vapors passing through without significant distortion of the sulfur dioxide cloud (45). Several fog nozzles may be situated farther downwind to absorb some of the remainder of the vapors getting through.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques discussed above, physical barriers such as buildings and rows of trees will help to contain the vapor cloud and control its movement. Hence, reducing the consequences of a hazardous vapor cloud can actually begin with a carefully planned layout of facilities and the use of imaginative landscaping around major hazard sites.

5.6 OPERATION AND MAINTENANCE PRACTICES

Accidental releases of toxic materials result not only from deficiencies of design but also from deficiencies of operation. Unfortunately, human error is often responsible for the realization of hazards with potentially damaging consequences. The human error hazard manifests itself in numerous ways, both indirectly and directly. For example, a lax management policy which does not enforce safety standards might be indirectly responsible for an unnecessary injury or fatality, or an operator may take the wrong action at a control panel which would directly lead to a hazardous release. Aspects of plant operation which impact the magnitude of the risk of human error include management policy, operator training, and maintenance and modification procedures. These topics are discussed in the following subsections.

5.6.1 Management Policy

Competent and effective management plays a vital role in the prevention of accidental releases as a result of human error. The primary responsibilities of managers at chemical plants with large inventories of hazardous chemicals include the following (39):

- Ensuring worker competency;
- Developing, documenting, and enforcing standard operating procedures and safety policies;
- Communicating and promoting feedback regarding safety issues;
- Identification, assessment, and control of hazards; and
- Regular plant audits and provisions for independent checks.

Management is ultimately responsible for the competency of workers hired at facilities which handle hazardous materials. Because of the serious consequences that may result from operator error at these installations, the qualifications and capabilities of prospective personnel for high hazard areas should be carefully assessed to ensure that worker skills are matched to job responsibilities. In addition, the skills of competent operators should be maintained by regular training, safety meetings, and employee reviews.

In the chemical industry, documentation is generally produced which sets forth standard procedures for equipment operation, maintenance, inspection, hazard identification, and emergencies. The enforcement of standard procedures is therefore one of management's most fundamental responsibilities in the area of plant safety and accident prevention. However, before procedures can be enforced, they must be communicated to plant personnel in a clear, concise style so that they are thoroughly understood. Emphasis should be placed on worker safety and the serious consequences of operator error in processes involving hazardous materials.

Unfortunately, requiring workers to read documents which contain safety policies is often not enough to ensure that they are fully understood and followed. For this reason, verbal communication should be practiced and encouraged which emphasizes plant safety and promotes feedback. When management demonstrates a willingness to respond to initiatives from below and participates directly with workers in improving safety, worker morale increases, influencing the degree to which standard procedures are followed.

Hazard identification, assessment, and control is another area that should be addressed by management to minimize the potential for accidental chemical releases. The establishment of formal hazard assessment techniques would provide management with a mechanism for obtaining information which can be used to rank potential problems and decide how best to allocate hazard control resources.

The plant safety audit is one of the most frequently used methods for obtaining safety related information. A total plant safety audit involves a thorough evaluation of a plant's design, layout, and procedures, and is specifically aimed at identifying and correcting potentially unsafe conditions. The objectives of these audits include alerting operating personnel to process hazards, determining if safety procedures need to be modified, screening for equipment or process changes that may have introduced new hazards, assessing the feasibility of applying new hazard control technologies, identifying additional hazards, and reviewing inspection and maintenance programs (47). In-house safety audits can be performed by appointed safety review committees, or qualified consultants or insurers may be brought in to provide a more objective assessment.

5.6.2 Operator Training

Accidental chemical releases may result from numerous types of operator errors including following incorrect operating procedures, failing to recognize critical situations, or by direct physical mistakes, e.g., by turning the wrong valve. For all of these errors, the fundamental problem may be the operator's lack of knowledge or understanding of process variables, equipment operation, or emergency procedures. It is important for management to recognize the extent to which a comprehensive operator training program can decrease the potential for accidental releases resulting from human error. Some general characteristics of quality industrial training programs include the following:

- Establishment of good working relations between management and personnel;
- Definition of trainer responsibilities and training program goals;
- Use of documentation, classroom instruction, and field training (in some cases supplemented with simulator training);
- Inclusion of procedures for normal startup and shutdown, routine operations, and emergencies; and
- Frequent supplemental training and the use of up-to-date training materials.

Employees in plants which manufacture, process, or store sulfur dioxide should be thoroughly educated about the important aspects of handling this chemical. These include the proper means of handling and storing, potential consequences of improper use and handling, prevention of spills, cleanup procedures, maintenance procedures, and emergency procedures. It is the job of the trainer to ensure that the right type and amount of information is supplied at the right time. To do this he must not only understand the technical content of a job, but also those aspects of the job where operators may have difficulty. It is therefore advantageous for trainers to spend time observing and analyzing the tasks and skills they will be teaching.

Two types of training which are especially important cover emergencies and safety procedures. Emergency training includes topics such as:

- Recognition of alarm signals;
- Performance of specific functions (e.g., shutdown switches);
- Use of emergency equipment;
- Evacuation procedures;
- Fire fighting; and
- Rehearsal of emergency situations.

Safety training includes not only responses to emergency situations, but also accident prevention measures. Aspects addressed in safety training sessions include (39):

- Hazard recognition and communication;
- Actions to be taken in particular situations;

- Available safety equipment and locations;
- When and how to use safety equipment;
- Use and familiarity with relevant documentation; and
- First aid and CPR.

The frequency of training and the frequency with which training materials are updated are important in maintaining strong training programs. Chemical processes may be modified to the extent that equipment changes require operational change, and operators must be made aware of the changes and safety considerations that accompany them in a timely manner. In addition to operator training programs, organized management training is also beneficial as it provides managers with the perspective necessary to formulate good policies and procedures and to make changes that will improve the quality of the overall plant safety program.

5.6.3 Maintenance and Modification Practices

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also potential causes of accidental chemical releases, proper maintenance and modification practices are important to the prevention of accidents.

Maintenance refers to a wide range of activities, including preventive maintenance, production assistance (e.g., adjustment of settings), servicing (e.g., lubrication and replacement of consumables), running maintenance, scheduled repairs during shutdown, and breakdown maintenance. These activities in turn require specific operations such as emptying, purging, and cleaning vessels, breaking pipelines, tank repair or demolition, welding, hot tapping (attaching a branch to an in-service line), and equipment removal (39).

Proper maintenance and modification programs should be a normal part of plant operation and design procedures, respectively, to reduce the chances for an accidental release. Maintenance should be based on a priority system to ensure that the most critical equipment is taken care of first. Strict procedures should apply to process modifications to ensure that modifications do not create unintended hazards. Inspections and nondestructive testing of vessels, piping, and machinery should be conducted periodically to detect small flaws that could eventually lead to a major release.

Two of the more common maintenance problems are equipment identification and equipment isolation (39). Work performed on the wrong piece of equipment can have disastrous effects, as can failure to completely isolate equipment from process materials and electrical connections. Other potential sources of maintenance accidents are improper venting to relieve pressure, insufficient draining, and not cleaning or purging systems before maintenance activities begin.

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed. Such permits generally include specific information such as (39):

- The type of maintenance operations to be conducted,
- Descriptions and identifying codes of the equipment to be worked on,
- Classification of the area in which work will be conducted,

- Documentation of special hazards and control measures,
- Listing of the maintenance equipment to be used, and
- The date and time when maintenance work will be performed.

Permit-to-work systems offer many advantages. They explain the work to be done to both operating and maintenance workers. In terms of equipment identification and hazard identification, they provide a level of detail that significantly reduces the potential for errors that could lead to accidents or releases. They also serve as historical records of maintenance activities.

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires which resulted in hazardous conditions, downtime, or direct repair costs.

One important maintenance practice is repairing or replacing equipment that appears to be headed for failure. A number of testing methods are available for examining the condition of equipment. Some of the most common types of tests are listed below.

- Metal thickness and integrity testing
- Vibration testing and monitoring
- Relief valve testing

All of the above testing procedures are nondestructive, i.e., they do not damage the material or equipment that they test.

Accidental releases are frequently the result of some aspect of plant modification. To avoid confusion with maintenance activities, a modification is defined as an intentional change in process materials, equipment, operating procedures, or operating conditions (39). Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. Frequently, hazards created by modifications do not appear in the exact location of the change. For example, equipment modifications can invalidate the arrangements for system pressure relief and blowdown or they can invalidate the function of instrumentation systems. Several factors should be considered in reviewing modification plans before authorizing work. According to Lees, these include (39):

- Sufficient number and size of relief valves,
- Appropriate electrical area classification,
- Elimination of effects which could reduce safety standards,
- Use of appropriate engineering standards,
- Proper materials of construction and fabrication standards,
- Existing equipment not stressed beyond design limits,
- Necessary changes in operating conditions, and

- Adequate instruction and training of operation and maintenance teams.

5.7 CONTROL EFFECTIVENESS

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, equipment design, and operational measures, are especially difficult to quantify because they reduce a probability rather than a physical quantity of a chemical release. Protective measures are more analogous to traditional pollution control technologies. Thus, they may be easier to quantify in terms of their efficiency in minimizing the adverse effects of a chemical that could be released.

Preventive measures reduce the probability of an accidental release by increasing the reliability of both process systems operations and the equipment. Control effectiveness can thus be expressed for both the qualitative improvements and the quantitative improvements through probabilities. Table 5-5 summarizes what appear to be some of the major design, equipment, and operational measures applicable to the primary hazards identified for the sulfur dioxide processes in the U.S. The items listed in this table are for illustration only and do not necessarily represent a satisfactory control option for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must therefore be evaluated individually. A discussion of reliability in terms of probabilities is planned for other parts of the prevention reference manual series.

5.8 ILLUSTRATIVE COST ESTIMATES FOR CONTROLS

This section presents cost estimates for different levels of control and for specific release prevention and protection measures for sulfur dioxide storage and process facilities found in the United States.

5.8.1 Prevention and Protection Measures

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Table 5-6 presents costs for some of the major design, equipment, and operational measures applicable to the primary hazards identified in Table 5-5 for the sulfur dioxide applications discussed in Section 3.

5.8.2 Levels of Control

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, and operation of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their costs. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. However, additional measures can be taken to provide extra protection against an accidental release.

The levels of control concept provides a means of assigning costs to increased levels of prevention and protection. At the lower end of the tier is the "Baseline" system. This system consists of the elements required for normal safe operation and basic prevention of an accidental release of hazardous material.

TABLE 5-5. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES FOR SULFUR DIOXIDE RELEASES

Hazard Area	Prevention/Protection
Water contamination in hydrocarbon feeds to extraction tower	Continuous moisture monitoring; Backflow prevention
Sulfur dioxide flow control	Redundant flow control loops; Minimal overdesign of feed systems
Temperature sensing and cooling medium flow control	Redundant temperature sensors; Interlock flow switch to shut off SO_2 feed on loss of cooling, with relief venting to emergency scrubber system
Temperature sensing and heating medium flow control	Redundant temperature sensors; Interlock flow switch to shut off SO_2 feed on loss of heating, with relief venting to emergency scrubber system
Overpressure	Redundant pressure relief; not isolatable; adequate size; discharge not restricted
Corrosion	Increased monitoring with more frequent inspections; use of pH sensing on cooling water and steam condensate loops; use of corrosion coupons; visual inspections; non-destructive testing
Reactor and reboiler temperatures	Redundant temperature sensing and alarms
Overfilling	Redundant level sensing, alarms and interlocks; training of operators
Atmosphere releases from relief discharges	Emergency vent scrubber system
Storage tank or line rupture	Enclosure vented to emergency scrubber system; diking; foams; dilution; neutralization; water sprays

TABLE 5-6. ESTIMATED TYPICAL COSTS OF MAJOR PREVENTION AND PROTECTION MEASURES FOR SULFUR DIOXIDE RELEASE[a]

Prevention/Protection Measure	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Continuous moisture monitoring	7500-10000	900-1300
Flow control loop	4000-6000	500-750
Temperature sensor	250-400	30-50
Pressure relief		
- relief valve	1000-2000	120-250
- rupture disk	1000-1200	120-150
Interlock system for flow shut-off	1500-2000	175-250
pH monitoring of cooling water	7500-10000	900-1300
Alarm system	250-500	30-75
Level sensor		
- liquid level gauge	1500-2000	175-250
- load cell	10000-15000	1300-1900
Diking		
- 3 ft high	1200-1500	150-175
- top of tank height, 10 ft.	7000-7500	850-900
Increased corrosion inspection[b]		200-400

[a] Based on a 10,000 gallon fixed sulfur dioxide storage tank system and a 200,000 gallon/day hydrocarbon extraction system.

[b] Based on 10-20 hr @ $20/hr.

The second level of control is "Level 1." "Level 1" includes the baseline system with added modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

The third level of control is "Level 2." This system incorporates both the "Baseline" and "Level 1" systems with additional modifications designed specifically for the prevention of an accidental release such as alarm and interlock systems. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures applied must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction along with proper operational practices are needed to assure safe operation.

Example "levels of control" cost estimates were prepared for a 42 ton fixed sulfur dioxide storage tank system with a 10,000 gal capacity and a sulfur dioxide extraction tower system for a 200,000 gal/day hydrocarbon extraction facility. These cost estimates are presented for illustrative purposes only. It is doubtful that any specific installation would find all of the control options listed in the following tables appropriate for their purposes. An actual system is likely to incorporate some items from each of the levels of control and also some control options not listed. The purpose of these estimates is to illustrate the relationship between cost and control, and not to provide an equipment check list.

5.8.3 Summary of Levels of Control

Table 5-7 presents a summary of the total capital and annual costs for each of the three levels of controls for the sulfur dioxide storage system and the sulfur dioxide extraction tower system. The costs presented correspond to the systems described in Table 5-8 and Table 5-9. Each of the level costs include the cost of the basic system plus any added controls. Specific cost information and breakdown for each level of control for both the storage and process facilities are presented in Tables 5-10 through 5-15.

5.8.4 Equipment Specifications and Detailed Costs

Equipment specifications and details of the capital cost estimates for the sulfur dioxide storage and the sulfur dioxide extraction tower systems are presented in Tables 5-16 through 5-23.

5.8.5 Methodology

Format for Presenting Cost Estimates--

Tables are provided for control schemes associated with storage and process facilities for sulfur dioxide showing capital, operating, and total annual costs. The tables are broken down into subsections comprising vessels, piping and valves, process machinery, instrumentation, and procedures and practice. The presentation of the costs in this manner allows for easy comparison of costs for specific items, different levels, and different systems.

Capital Cost--All capital costs presented in this report are shown as total fixed capital costs. Table 5-24 defines the cost elements comprising total fixed capital as it is used here.

The computation of total fixed capital as shown in Table 5-24 begins with the total direct cost for the system under consideration. This total direct cost is the total direct installed cost of all capital equipment comprising

TABLE 5-7. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR SULFUR DIOXIDE STORAGE TANK AND EXTRACTION TOWER

	Level of Control	Total Capital Cost (1986 $)	Total Annual Cost (1986 $/yr)
Sulfur Dioxide Tank 63 ton Fixed SO_2 Tank with 10,000 gal Capacity	Baseline	186,000	22,000
	Level #1	549,000	65,000
	Level #2	1,360,000	160,000
Sulfur Dioxide Extraction Tower System with 5 ft x 20 ft Packed Tower	Baseline	189,000	24,000
	Level #1	548,000	68,000
	Level #2	780,000	95,000

TABLE 5-8. EXAMPLE OF LEVELS OF CONTROL FOR SULFUR DIOXIDE STORAGE TANK

Process: 63 ton fixed sulfur dioxide storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Process:	None	None	None
Flow:	Single check-valve on tank-process feed line.	Add second check valve.	Add a reduced-pressure device[a] with internal air gap and relief vent to containment tank or scrubber.
Temperature:	None	None	Add temperature indicator.
Pressure:	Single pressure relief valve, vent to atmosphere.	Add second relief valve, secure non-isolatable. Vent to limited scrubber. Provide local pressure indicator.	Add rupture disks under relief valves. Provide local pressure indication on space between disk and valve.
Quantity:	Local level indicator.	Add remote level indicator.	Add level alarm. Add high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic.	Away from traffic and flammables.	Away from traffic, flammables, and other hazardous processes.
Materials of Construction:	Carbon steel	Carbon steel with increased corrosion allowances. (1/8 inch)	Stainless steel, Type 316.
Vessel:	Tank pressure specification 150 psig.	Tank pressure specification 225 psig.	Tank pressure specification 375 psig.

(Continued)

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[a] A reduced pressure device is a modified double check valve.

TABLE 5-8 (Continued)

Process: 63 ton fixed sulfur dioxide storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Sch. 80 carbon steel.	Sch. 80 316 SS	Sch. 80 Alloy 20 SS
Process Machinery:	Centrifugal pump, carbon steel, stuffing box seal.	Centrifugal pump, 316 SS construction, double capacity mechanical seal.	Magnetically-couple centrifugal pump, 316 SS, construction.
Enclosures:	None	Steel building.	Concrete building.
Diking:	None	3 ft. high.	Top of tank height.
Scrubbers:	None	Water scrubber.	Alkaline scrubber.
Mitigation:	None	Water sprays.	Alkaline water sprays and barriers.

TABLE 5-9. EXAMPLE OF LEVELS OF CONTROL FOR SULFUR DIOXIDE EXTRACTION TOWER

Controls	Baseline	Level #1	Level #2
Process:	Dryers on feed lines.	Enchanced flow control.	Operate tower at lower temperature.
Temperature:	Local temperature indicator.	Add redundant sensors and alarm.	Add remote indicator.
Pressure:	None	None	None
Flow:	Flow control of sulfur dioxide feed.	Redundant flow control loop.	Add interlock system to shutoff sulfur dioxide feed upon reaching a temperature above a set point.
Quantity:	Local level control.	Add level alarm.	Same
Corrosion:	Visual inspection and monitoring.	Increased monitoring with increased inspections.	Same
Composition:	Dryers on hydrocarbon charge and SO_2 feed lines.	Occasional moisture monitoring. Add moisture alarms on SO_2 and hydrocarbon feed.	Continuous moisture monitoring
Material of Construction:	Carbon-steel	Acid brick lined carbon steel.	Type 316 stainless-steel.
Vessel	Tank pressure specification 50 psig.	Tank pressure specification 100 psig.	Tank pressure specification 150 psig.

(Continued)

TABLE 5-9 (Continued)

Controls	Baseline	Level #1	Level #2
Piping:	Sch. 80 carbon steel.	Sch. 80 Type 316 stainless steel.	Sch. 80 Alloy 20 stainless steel.
Process Machinery:	Centrifugal pump with stuffing box, carbon steel construction.	Centrigual pump, double mechanical seal, Type 316 stainless steel construction.	Magnetically-coupled centrifugal pump, Type 316 stainless steel construction.
Protective Barrier:	None	Curbing around tower.	3 ft. high retaining wall.
Enclosures	None	Steel building.	Concrete building.
Scrubbers:	None	Water scrubber.	Alkaline scrubber.
Mitigation:	None	Water sprays.	Alkaline water sprays.

TABLE 5-10. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE SULFUR DIOXIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage tank	131,000	15,000
Expansion tanks (3)	6,500	760
Piping and Valves:		
Pipework	9,200	1,100
Check valve	1,000	120
Ball valves (5)	6,200	720
Excess flow valves (2)	1,900	220
Angle valves (2)	7,500	870
Relief valve	2,000	230
Process Machinery:		
Centrifugal pump	18,000	2,100
Instrumentation:		
Pressure gauges (4)	1,500	180
Liquid level gauge	1,500	180
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		15
Piping inspection		300
Piping maintenance		120
Valve inspection		30
Valve maintenance		350
Total Costs	186,000	22,000

TABLE 5-11. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 SULFUR DIOXIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage tank	190,000	22,000
Expansion tanks (3)	6,500	760
Piping and Valves:		
Pipework	30,000	3,500
Check valve	2,000	240
Ball valves (5)	6,200	720
Excess flow valves (2)	1,900	220
Angle valves (2)	7,500	870
Relief valve	4,000	460
Process Machinery:		
Centrifugal pump	35,000	4,000
Instrumentation:		
Pressure gauges (4)	1,500	180
Flow indicator	3,700	430
Load cell	1,500	180
Remote level indicator	1,900	220
Enclosures:		
Steel building	10,000	1,200
Scrubbers:		
Water scrubber	249,000	29,000
Diking:		
3 ft high concrete diking	1,400	160

(Continued)

TABLE 5-11 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		30
Piping inspection		300
Piping maintenance		120
Valve inspection		35
Valve maintenance		400
Total Costs	549,000	65,000

TABLE 5-12. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 SULFUR DIOXIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Storage tank	879,000	102,000
Expansion tanks (3)	6,500	760
Piping and Valves:		
Pipework	49,000	5,700
Reduced pressure device	5,000	590
Ball valves (5)	6,200	720
Excess flow valves (2)	1,900	220
Angle valves (2)	7,500	870
Relief valve	4,000	460
Rupture disks (2)	1,100	130
Process Machinery:		
Centrifugal pump	43,000	5,000
Instrumentation:		
Temperature indicator	2,200	260
Pressure gauges (6)	2,200	260
Flow indicator	3,700	440
Load cell	16,000	1,800
Remote level indicator	1,900	220
Level alarm	750	90
High-low level shutoff	1,900	220
Enclosures:		
Concrete building	19,000	2,200
Scrubbers:		
Alkaline scrubber	302,000	35,000
Diking:		
10 ft. high diking	7,500	870

(Continued)

TABLE 5-12 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		50
Piping inspection		300
Piping maintenance		120
Valve inspection		35
Valve maintenance		400
Total Costs	1,360,000	160,000

TABLE 5-13. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Equipment:		
Extraction tower	56,000	6,800
Tower packing	35,000	4,200
Expansion tank	2,500	300
Piping and Valves:		
Pipework	27,000	3,200
Ball valves (8)	13,000	1,600
Process Machinery:		
Centrifugal pumps (2)	35,000	4,200
Instrumentation:		
Pressure gauges (3)	1,100	130
Liquid level control		
- Controller	1,800	220
- Sensor	2,200	260
- Control valve	4,500	540
Local temp. indicator	2,200	260
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	4,500	540
Maintenance and Inspections:		
Visual tower inspection (external)		15
Visual tower inspection (internal)		60
Piping inspection		900
Piping maintenance		360
Valve inspection		30
Valve maintenance		350
Total Costs	189,000	24,000

TABLE 5-14. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Equipment:		
Extraction tower	65,000	7,800
Tower packing	35,000	4,100
Expansion tank	2,500	300
Piping and Valves:		
Pipework	85,000	10,000
Ball valves (8)	13,000	1,600
Process Machinery:		
Centrifugal pumps (2)	66,000	8,000
Instrumentation:		
Pressure gauges (3)	1,100	130
Level alarm	360	45
Liquid level control		
- Controller	1,800	220
- Sensor	2,200	260
- Control valve	4,500	540
Local temp. indicator	2,200	260
Temperature sensor	360	45
Temperature alarm	360	45
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	4,500	540
Addition flow control loop	9,000	1,100
Moisture alarm	360	45

(Continued)

TABLE 5-14 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Diking:		
Curbing around tower	1,200	150
Enclosure:		
Steel building	10,000	1,200
Scrubber:		
Water scrubber	240,000	29,000
Maintenance and Inspections:		
Visual tower inspection (external)		15
Visual tower inspection (internal)		60
Piping inspection		900
Piping maintenance		360
Valve inspection		30
Valve maintenance		350
Total Costs	548,000	68,000

TABLE 5-15. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Vessels:		
Extraction tower	205,000	25,000
Tower packing	35,000	4,100
Expansion tank	2,500	300
Piping and Valves:		
Pipework	85,000	10,000
Ball valves (8)	13,000	1,600
Process Machinery:		
Centrifugal pumps (2)	83,000	10,000
Instrumentation:		
Pressure gauges (3)	1,100	130
Level alarm	360	45
Liquid level control		
- Controller	1,800	220
- Sensor	2,200	260
- Control valve	4,500	540
Local temp. indicator	2,200	260
Remote temp. indicator	1,800	220
Temperature sensor	360	45
Temperature alarm	360	45
Flow interlock system	1,800	220
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	4,500	540

(Continued)

TABLE 5-15 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Additional flow control loop	9,000	1,100
Moisture alarm	360	45
Moisture monitoring system	9,000	1,100
Diking:		
3 ft. high retaining wall	3,100	370
Enclosure:		
Concrete building	18,000	2,200
Scrubber:		
Alkaline scrubber	292,000	35,000
Maintenance and Inspections:		
Visual tower inspection (external)		15
Visual tower inspection (internal)		60
Piping inspection		900
Piping maintenance		360
Valve inspection		30
Valve maintenance		350
Total Costs	780,000	95,000

TABLE 5-16. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH SULFUR DIOXIDE STORAGE SYSTEM

Equipment Item	Equipment Specification	Reference
Vessels:		
Storage tank	Baseline: 10,000 gal. carbon steel storage tank 150 psig rating	
	Level 1: 10,000 gal. carbon steel with 1/8 in. corrosion protection, 225 psig rating	48, 49
	Level 2: 10,000 gal. Type 316 stainless steel 375 psig rating	50, 51
Expansion tank	Standard carbon steel pressure vessel with rupture disk and pressure gauge	48, 49
Piping and Valves:	Baseline: 100 ft. of 4 in. schedule 80 carbon steel	
Pipework	Level 1: 100 ft. of 4 in. schedule 80 Type 316 stainless steel	
	Level 2: 100 ft. of 4 in. schedule 80 Alloy 20	51
Ball valve	4 in., Class 300, flanged, Type 316 stainless steel construction	49, 53
Check valve	4 in., Class 300, vertical lift, Type 316 stainless steel	49, 53
Excess flow valve	4 in. standard valve	49
Angle valve	4 in., Type 316 stainless steel	54

(Continued)

TABLE 5-16 (Continued)

Equipment Item	Equipment Specification	Reference
Relief valve	1 in. x 2 in., Class 300 inlet and outlet flange, angle body, closed bonnet with screwed cap, Type 316 stainless steel body and trim	49
Reduced pressure device	Double check valve type device with internal air gap and relief valve	48
Rupture disk	1 in. Type 316 stainless steel and carbon steel holder	50, 55, 56
Process Machinery:		
Centrifugal pump	Baseline: single stage, carbon steel construction, stuffing box	
	Level 1: single stage, Type 316 stainless steel construction, double mechanical seal	49, 57
	Level 2: Type 316 stainless steel construction, magnetically-coupled	48, 49, 52
Instrumentation:		
Temperature indicator	Thermocouple, thermowell, electronic indicator	48, 49, 52
Pressure gauge	Diaphragm sealed, Type 316 stainless steel diaphragm, 0-1,000 psig	58, 52
Liquid level gauge	Differential pressure type level gauge	

(Continued)

TABLE 5-16 (Continued)

Equipment Item	Equipment Specification	Reference
Flow indicator	Differential pressure cell, transmitter, and associated flowmeter	48, 52
Level indicator	Electronic differential pressure type indicator	48, 49, 52
Load cell	Electronic load cell	48, 52, 58
Level alarm	Indicating and audible alarm	49, 54, 59
High-low level shutoff	Solenoid valve, switch, and relay system	48, 49, 52 54
Enclosures:		
Building	Level 1: 26 gauge steel walls and roof, door, ventilation system	
	Level 2: 10 in. concrete walls, 26 gauge steel roof	54
Scrubbers:	Level 1: Spray tower, Type 316 stainless steel construction, water sprays, 8 ft. x 24 ft.	
	Level 2: Spray tower, Type 316 stainless steel construction, alkaline sprays	60
Diking:	Level 1: 6 in. concrete walls, 3 ft. high	
	Level 2: 10 in. concrete walls, top of tank height	54

TABLE 5-17. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE SULFUR DIOXIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage tank	61,000	27,000	88,000	31,000	131,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
Piping and Valves:					
Pipework	2,300	3,900	6,200	2,200	9,200
Check valves	640	30	670	230	1,000
Ball valves (5)	4,000	150	4,150	1,500	6,200
Excess flow valves (2)	1,200	40	1,240	440	1,900
Angle valves (2)	5,000	40	5,040	1,800	7,500
Relief valve	1,300	50	1,350	470	2,000
Process Machinery:					
Centrifugal pump	8,500	3,600	12,100	4,200	18,000
Instrumentation:					
Pressure gauges (4)	800	200	1,000	350	1,500
Liquid level gauge	800	200	1,000	350	1,500
Total Costs	89,000	36,000	125,000	44,000	186,000

TABLE 5-18. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 SULFUR DIOXIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage tank	88,000	40,000	128,000	45,000	190,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
Piping and Valves:					
Pipework	15,000	5,000	20,000	7,000	30,000
Check valves (2)	1,300	60	1,360	480	2,000
Ball valves (5)	4,000	150	4,150	1,500	6,200
Excess flow valves (2)	1,200	40	1,240	440	1,900
Angle valves (2)	5,000	40	5,040	1,800	7,500
Relief valves (2)	2,600	100	2,700	940	4,000
Process Machinery:					
Centrifugal pump	16,000	7,000	23,000	8,100	35,000
Instrumentation:					
Pressure gauges (4)	800	200	1,000	350	1,500
Flow indicator	2,000	500	2,500	880	3,700
Liquid level gauge	800	200	1,000	350	1,500
Remote level indicator	1,000	250	1,250	440	1,900
Enclosures:					
Steel building	4,600	2,300	6,900	2,400	10,000

(Continued)

TABLE 5-18 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Scrubbers:					
Water scrubber	115,000	52,000	167,000	59,000	249,000
Diking:					
3 ft. high concrete diking	390	520	910	320	1,400
Total Costs	261,000	109,000	370,000	130,000	549,000

TABLE 5-19. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 SULFUR DIOXIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Vessels:					
Storage tank	408,000	184,000	592,000	207,000	879,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
Piping and Valves:					
Pipework	28,000	5,000	33,000	12,000	49,000
Reduced pressure device	3,200	200	3,400	1,200	5,000
Ball valves (5)	4,000	150	4,150	1,500	6,200
Excess flow valves (2)	1,200	40	1,240	440	1,900
Angle valves (2)	5,000	40	5,040	1,800	7,500
Relief valve	2,600	100	2,700	940	4,000
Rupture disks (2)	650	75	725	260	1,100
Process Machinery:					
Centrifugal Pump	20,000	9,000	29,000	10,000	43,000
Instrumentation:					
Temperature indicator	1,200	300	1,500	530	2,200
Pressure gauges (6)	1,200	300	1,500	530	2,200
Flow indicator	2,000	500	2,500	880	3,700
Load cell	8,400	2,100	10,500	3,700	16,000
Remote level indicator	1,000	250	1,250	440	1,900
Level alarm	400	100	500	180	750
High-low level shutoff	1,000	250	1,250	440	1,900

(Continued)

TABLE 5-19 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Enclosures:					
Concrete building	6,100	6,600	12,700	4,500	19,000
Scrubbers:					
Alkaline scrubber	140,000	63,000	203,000	71,000	302,000
Diking:					
10 ft. high diking	2,200	2,900	5,100	1,800	7,500
Total Costs	640,000	276,000	916,000	321,000	1,360,000

TABLE 5-20. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

Equipment Item	Equipment Specification	Reference
Vessels:		
Extraction tower	Baseline: 5 ft. x 20 ft. packed tower, carbon steel construction, 50 psig rating Level 1: Acid brick lined carbon steel construction, 100 psig rating Level 2: Type 316 stainless steel construction, 150 psig rating	48
Tower packing	1-3/4 in. Type 316 stainless steel Raschig rings at a depth of 10 ft.	48
Expansion tank	Standard carbon steel pressure vessel with rupture disk and pressure gauge	48,49
Piping and Valves:		
Pipework	Baseline: 300 ft. of 4" schedule 80 carbon steel Level 1: 4in. schedule 80 Type 316 stainless steel Level 2: 4 in. schedule 80 alloy 20 stainless steel	52
Ball valves	4 in., Class 300, flanged, Type 316 stainless steel construction	49, 53
Process Machinery:		
Centrifugal pump	Baseline: single stage, carbon steel construction, stuffing box Level 1: single stage, Type 316 stainless steel construction, double mechanical seal	49, 57

(Continued)

TABLE 5-20 (Continued)

Equipment Item	Equipment Specification	Reference
Centrifugal Pump	Level 2: Type 316 stainless steel construction, magnetically-coupled	49, 57
Instrumentation:		
Pressure gauge	Diaphragm sealed, Type 316 stainless steel diaphragm, 0-1,000 psig rating	48, 49, 52
Level alarm	Indicating and audible alarm	
Liquid level control loop	PID controller, 4 in. globe control valve of stainless steel construction, gravity differential sensor system	48, 52
Local temperature indicator	Thermocouple, thermowell, and electronic indicator	48, 49, 52
Remote temperature indicator	Transmitter and associated electronic indicator	48, 52
Temperature sensor	Thermocouple and associated thermowell	48, 49, 52
Temperature alarm	Indicating and audible alarm	49, 54, 59
Flow interlock system	Solenoid valve, switch, and relay system	48, 49, 52 54
Flow control loop	PID controller, 4" globe control valve of stainless steel construction, flowmeter	48, 52
Moisture alarm	Moisture sensor and indicating and audible alarm	58

(Continued)

TABLE 5-20 (Continued)

Equipment Item	Equipment Specification	Reference
Moisture Monitoring System	Capacitance or Infrared absorption system	
Diking:	Level 1: 0.5 ft. high concrete curbing Level 2: 3 ft. high concrete retaining wall	
Enclosure:	Level 1: 26 gauge steel walls and roof, door, ventilation system Level 2: 0.8 ft. concrete walls, 26 gauge steel roof	
Scrubber:	Level 1: Spray tower, Type 316 stainless steel construction, water sprays, 8 ft. x 24 ft. Level 2: Spray tower, Type 316 stainless steel construction, alkaline sprays	

TABLE 5-21. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Extraction tower	27,000	12,000	39,000	9,800	56,000
Tower packing	17,000	7,400	24,400	6,100	35,000
Expansion tank	1,200	540	1,740	440	2,500
Piping and Valves:					
Pipework	6,800	12,000	18,800	4,700	27,000
Ball valves (8)	8,000	1,200	9,200	2,300	13,000
Process Machinery:					
Centrifugal pumps (2)	17,000	7,200	24,200	6,100	35,000
Instrumentation:					
Pressure gauges (3)	600	150	750	190	1,100
Liquid level control					
- Controller	1,000	250	1,250	320	1,800
- Sensor	1,200	300	1,500	380	2,200
- Control valve	2,500	630	3,130	780	4,500
Local temp. indicator	1,200	300	1,500	380	2,200
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	330	1,630	410	2,300
- Control valve	2,500	630	3,130	780	4,500
Total Costs	88,000	43,000	131,000	33,000	189,000

TABLE 5-22. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Extraction tower	31,000	14,000	45,000	11,000	65,000
Tower packing	17,000	7,400	24,400	6,100	35,000
Expansion tank	1,200	540	1,740	440	2,500
Piping and Valves:					
Pipework	44,000	15,000	59,000	15,000	85,000
Ball valves (8)	8,000	1,200	9,200	2,300	13,000
Process Machinery:					
Centrifugal pumps (2)	32,000	14,000	46,000	12,000	66,000
Instrumentation:					
Pressure gauges (3)	600	150	750	190	1,100
Level alarm	200	50	250	65	360
Liquid level control					
- Controller	1,000	250	1,250	320	1,800
- Sensor	1,200	300	1,500	380	2,200
- Control valve	2,500	630	3,130	780	4,500
Local temperature indicator	1,200	300	1,500	380	2,200

(Continued)

TABLE 5-22 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Temperature sensor	200	50	250	65	360
Temperature alarm	200	50	250	65	360
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	330	1,630	410	2,300
- Control valve	2,500	630	3,130	780	4,500
Additional flow control loop	4,800	1,210	6,010	1,600	9,000
Moisture alarm	200	50	250	65	360
Diking:					
Curbing around tower	500	350	850	220	1,200
Enclosure:					
Steel building	4,600	2,300	6,900	1,700	10,000
Scrubber:					
Water scrubber	115,000	52,000	167,000	42,000	240,000
Total Costs	270,000	111,000	381,000	96,000	548,000

TABLE 5-23. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 SULFUR DIOXIDE EXTRACTION TOWER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Equipment:					
Extraction tower	98,000	44,000	142,000	36,000	205,000
Tower packing	17,000	7,400	24,400	6,100	35,000
Expansion tank	1,200	540	1,740	440	2,500
Piping and Valves:					
Pipework	44,000	15,000	59,000	15,000	85,000
Ball valves (8)	8,000	1,200	9,200	2,300	13,000
Process Machinery:					
Centrifugal pumps (2)	40,000	18,000	58,000	15,000	83,000
Instrumentation:					
Pressure gauges (3)	600	150	750	190	1,100
Level alarm	200	50	250	65	360
Liquid level control					
- Controller	1,000	250	1,250	320	1,800
- Sensor	1,200	300	1,500	380	2,200
- Control valve	2,500	630	3,130	780	4,500

(Continued)

TABLE 5-23 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Local temp. indicator	1,200	300	1,500	380	2,200
Remote temp. indicator	1,000	250	1,250	320	1,800
Temperature sensor	200	50	250	65	360
Temperature alarm	200	50	250	65	360
Flow interlock sytem	1,000	250	1,250	320	1,800
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	325	1,625	410	2,300
- Control valve	2,500	625	3,125	780	4,500
Additional flow control loop	4,800	1,210	6,010	1,600	9,000
Moisture alarm	200	50	250	65	360
Moisture monitoring system	5,000	1,250	6,250	1,600	9,000
Diking:					
3 ft. high retaining wall	900	1,200	2,100	530	3,100
Enclosure:					
Concrete building	6,000	6,600	12,600	3,200	18,000

(Continued)

TABLE 5-23 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
Scrubber:					
Alkaline scrubber	140,000	63,000	203,000	51,000	292,000
Total Costs	379,000	163,000	542,000	135,000	780,000

TABLE 5-24. FORMAT FOR TOTAL FIXED CAPITAL COST

Item No.	Item	Cost
1	Total Material Cost	-
2	Total Labor Cost	-
3	Total Direct Cost	Items 1 + 2
4	Indirect Cost Items (Engineering & Construction Expenses)	0.35 x Item 3[a]
5	Total Bare Module Cost	Items (3 + 4)
6	Contingency	(0.05 x Item 5)[b]
7	Contractor's Fee	0.05 x Item 5
8	Total Fixed Capital Cost	Items (5 + 6 + 7)

[a] For storage facilities, the indirect cost factor is 0.35. For process facilities, the indirect cost factor is 0.25.

[b] For storage facilities, the contingency cost factor is 0.05. For process facilities, the contingency cost factor is 0.10.

the system. Depending on the specific equipment item involved, the direct capital cost was available or was derived from uninstalled equipment costs by computing costs of installation separately. To obtain the total fixed capital cost, other costs obtained by utilizing factors are added to the total direct costs.

The first group of other cost elements is indirect costs. These include engineering and supervision, construction expenses, and various other expenses such as administration expenses, for example. These costs are computed by multiplying total direct costs by a factor shown in Table 5-24. The factor is approximate, is obtained from the cost literature, and is based on previous experience with capital projects of a similar nature. Factors can have a range of values and vary according to technology area and for individual technologies within an area. Appropriate factors were selected for use in this report based on judgement and experience.

When the indirect costs are added to the total direct costs, total bare module cost is obtained. Some additional cost elements such as contractor's fee and contingency are calculated by applying and adding appropriate factors to the total bare module cost as shown in Table 5-24 to obtain the total fixed capital cost.

Annual Cost--Annual costs are obtained for each of the equipment items by applying a factor for both capital recovery and for maintenance expenses to the direct cost of each equipment item. Table 5-25 defines the cost elements and appropriate factors comprising these costs. Additional annual costs are incurred for procedural items such as valve and vessel inspections, for example. When all of these individual costs are added, the total annual cost is obtained.

TABLE 5-25. FORMAT FOR TOTAL ANNUAL COST

Item No.	Item	Cost
1	Total Direct Cost	-
2	Capital Recovery on Equipment Items	0.163 x Item 1
3	Maintenance Expense on Equipment Items	0.01 x Item 1
4	Total Procedural Items	-
5	Total Annual Cost	Items (2 + 3 + 4)

Sources of Information--

The costs presented in this report are derived from cost information in existing published sources and also from recent vendor information. It was the objective of this effort to present cost levels for sulfur dioxide process and storage facilities using the best costs for available sources. The primary sources of cost information are Peters and Timmerhaus (48), Chemical Engineering (61), and Valle-Riestra (62) supplemented by other sources and references where necessary. Adjustments were made to update all costs to a June 1986 dollar basis. In addition, for some equipment items, well-documented costs were not available and they had to be developed from component costs.

Costs in this document reflect the "typical" or "average" representation for specific equipment items. This restricts the use of data in this report to:

- Preliminary estimates used for policy planning.
- Comparison of relative costs of different levels or systems, and
- Approximations of costs that might be incurred for a specific application.

The costs in this report are considered to be "order of magnitude" with a ±50 percent margin. This is because the costs are based on preliminary estimates and many are updated from literature sources. Large departures from the design basis of a particular system presented in this manual or the advent of a different technology might cause the system cost to vary by a greater extent than this. If used as intended, however, this document will provide a reasonable source of preliminary cost information for the facilities covered.

When comparing costs in this manual to costs from other references, the user should be sure the design bases are comparable and that the capital and annual costs as defined here are the same as the costs being compared.

Cost Updating--

All costs in this report are expressed in June 1986 dollars. Costs reported in the literature were updated using cost indices for materials and labor.

Costs expressed in base year dollars may be adjusted to dollars for another year by applying cost indices as shown in the following equation:

$$\text{new base year cost} = \text{old base year cost} \times \frac{\text{new base year index}}{\text{old base year index}}$$

The Chemical Engineering (CE) Plant Cost Index was used in updating cost for this report. For June 1986, the index is 316.3.

Equipment Costs--

Most of the equipment costs presented in this manual were obtained directly from literature sources of vendor information and correspond to a specific design standard. Special cost estimating techniques, however, were used in determining the costs associated with vessels, piping systems, scrubbers, diking, and enclosures. The techniques used are presented in the following subsections of this manual.

Vessels--The total purchased cost for a vessel, as dollars per pound of weight of fabricated unit f.o.b. with carbon steel as the basis (January 1979 dollars) was determined using the following equation from Peters and Timmerhaus (48):

$$\text{Cost} = [50(\text{Weight of Vessel in Pounds})^{-0.34}]$$

The vessel weight is determined using appropriate design equations as given by Peters and Timmerhaus (48) which allow for wall thickness adjustments for corrosion allowances, for example. The vessel weight is increased by a factor of 0.15 for horizontal vessels and 0.20 for vertical vessels to account for the added weight due to nozzles, manholes, and skirts or saddles. Appropriate factors are applied for different materials of construction as given in Peters and Timmerhaus (48). The vessel costs are updated using cost factors. Finally a shipping cost amounting to 10 percent of the purchased cost is added to obtain the delivered equipment cost.

Piping--Piping costs were obtained using cost information and data presented by Yamartino (63). A simplified approach is used in which it is assumed that a certain length of piping containing a given number of valves, flanges, and fittings is contained in the storage or process facility. the data presented by Yamartino (63) permit cost determinations for various lengths, sizes, and types of piping systems. Using these factors, a representative estimate can be obtained for each of the storage and process facilities.

Diking--Diking costs were estimated using Mean's Manual (54) for reinforced concrete walls. The following assumptions were made in determining the costs. The dike contains the entire contents of a tank in the event of a leak or release. Two dike sizes are possible: a three-foot high dike, six-inches thick and a top-of-tank height dike ten inches thick. The tanks are raised off the ground and are not volumetrically included in the volume enclosed by the diking. These assumptions facilitate cost determination for any size diking system.

Enclosures--Enclosure costs were estimated using Mean's Manual (54) for both reinforced concrete and steel-walled buildings. The buildings are assumed to enclose the same area and volume as the top-of-tank height dikes. The concrete building is ten inches thick with a 26-gauge steel roof and a metal door. The steel building has 26 gauge roofing and siding and metal door. The cost of a ventilation system was determined using a typical 1,000 scfm unit and doubling the cost to account for duct work and requirements for the safe enclosure of hazardous chemicals.

Scrubbers--Scrubber costs were estimated using the following equation from the Gard (60) manual for spray towers based on the actual cubic feet per minute of flow at a chamber velocity of 600 feet/min.

$$\text{Costs} = 0.235 \times (\text{ACFM} + 43,000)$$

A release rate of 10,000 ft^3/min was assumed for the storage vessel systems and an appropriate rate was determined for the process system based on the quantity of hazardous chemicals present in the system at any one time. For the sulfur dioxide extraction tower system, a release rate of 10,000 ft^3/min was assumed. In addition to the spray tower, the costs also include pumps and a storage tank for the scrubbing medium. The costs presented are updated to June 1986 dollars.

Installation Factors--

Installation costs were developed for all equipment items included in both the process and storage systems. The costs include both the material and labor costs for installation of a particular piece of equipment. The costs were obtained directly from literature sources and vendor information or indirectly by assuming a certain percentage of the purchased equipment cost through the use of estimating factors obtained from Peters and Timmerhaus (48) and Valle-Riestra (62). Table 5-26 lists the cost factors used or the reference from which the cost was obtained directly. Many of the costs obtained from the literature were updated to June 1986 dollars using a 10 percent per year rate of increase for labor and cost indices for materials associated with installation.

TABLE 5-26. FORMAT FOR INSTALLATION COSTS

Equipment Item	Factor or Reference
Vessels:	
Storage Tank	0.45
Expansion Tank	0.25
Piping and Valves:	
Pipework	Ref. 63
Expansion Loop	Ref. 49
Reduced Pressure Device	Ref. 49
Check Valves	Ref. 49
Gate Valves	Ref. 49
Ball Valves	Ref. 49
Excess Flow Valves	Ref. 49
Angle Valves	Ref. 54
Relief Valves	Ref. 49
Rupture Disks	Ref. 49
Process Machinery:	
Centrifugal Pump	0.43
Gear Pump	0.43
Instrumentation:	
All Instrumentation Items	0.25
Enclosures:	Ref. 54
Diking:	Ref. 54
Scrubbers:	0.45

SECTION 6

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APPENDIX A

GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Cavitation: The formation and collapse of vapor bubbles in a flowing liquid. Specifically the formation and collapse of vapor cavities in a pump when there is sufficient resistance to flow at the inlet side.

Creep failure: Failure of a piece of metal as a result of creep. Creep is time dependent deformation as a result of stress. Metals will deform when exposed to stress. High levels of stress can result in rapid deformation and rapid failure. Lower levels of stress can result in slow deformation and protracted failure.

Deadheading: Closing or nearly closing or blocking the discharge outlet or piping of an operating pump or compressor.

Electromotive Series of Metals: A list of metals and alloys arranged according to their standard electrode potentials; which also reflects their relative corrosion potential.

Enthalpy: A thermodynamic property of a chemical related to its energy content at a given condition of temperature, pressure and physical state. Enthalpy is the internal energy added to the product of pressure times volume. Numerical values of enthalpy for various chemicals are always based on the change in enthalpy from an arbitrary reference pressure and temperature, and physical state, since the absolute value cannot be measured.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Hygroscopic: Readily absorbing and retaining moisture, usually in reference to readily absorbing moisture from the air.

Mild steel: Carbon steel containing a maximum of about 0.25% carbon. Mild steel is satisfactory for use where severe corrodants are not encountered or where protective coatings can be used to prevent or reduce corrosion rates to acceptable levels.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Passivation film: A layer of oxide or other chemical compound of a metal on its surface that acts as a protective barrier against corrosion or further chemical reaction.

Plant: A location at which a process or set of processes are used to produce, refine, or repackage, chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Process: The sequence of physical and chemical operations for the production, refining, repackaging or storage of chemicals.

Process machinery: Process equipment, such as pumps, compressors, heaters, or agitators, that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B
TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	(psig+14.696)x(6.895)
Temperature:	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value:	Btu/lb	kJ/kg	2.326
Enthalpy:	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentration:	oz/gal	kg/m^3	7.490
	quarts/gal	cm^3/m^3	25,000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	kg/m-s	0.001

*Calculate as indicated